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Full and Partial Polarization Switching Characteristics of Sol-Gel derived Pb(ZrxTi1-x)O3 Thin Films

Joon Han Kim, and Chang Yub Park
Dept. of Electrical Eng., Yonsei University
Shinchon-dong, Seodaemun-gu, Seoul, Korea

ABSTRACT

In this study, polarization switching characteristics of Pb(ZrxTi1-x)O3 (PZT) thin films were investigated. Switching times(ts) were found to be decreased as the Zr mol% was increased. But, the switching peak currents(Imax) showed the largest value at 50 mol% Zr. As a result of this experiment, ts was found to be depended on the remanent polarization and coercive field and also Imax strongly depended on the dielectric constant of PZT thin films. In order to investigate the partial switching kinetics of PZT thin films, short and relatively small voltage pulses were applied to the MFM (metal ferroelectric metal) PZT capacitors and polarization switching curves were measured with a variation of the total width of the applied pulses. Also, the switching curves were measured at different applied voltages(4, 8, 10, 12, and 14 volts). As the applied voltages increased, ts and Imax were found to be decreased and increased, respectively. In case of fatigued specimen which we applied ±10 volts square pulse for 10_{10} cycles, ts and Imax were found to be shorter and smaller than those of virgin specimens. This is due to the decrease of the remanent polarization and the increase of the coercive field.

Key words : PZT thin film, sol-gel processing, polarization switching, fatigue, remanent polarization, ferroelectric memory

1. Introduction

In recent years there has been a surge in research activity on lead zirconate titanate(PZT) films for memory applications.[1,2,3] In ferroelectric memory applications, memorized information of the devices can be determined by the state of the remanent polarization in ferroelectric thin films. There are many important characteristics of PZT thin films for memory applications such as hysteresis, polarization switching, fatigue, imprint, and so on. The polarization switching is one of the most important characteristics for ferroelectric memory devices because the access time of the memory devices is strongly depend upon the polarization switching time. Ferroelctic thin films can be used as a charge storage capacitor which has MFM(metal-ferroelectric-metal) capacitor structure and also a gate oxide insulator for FET devices such as MFS(metal-ferroelecric-semiconductor) or MFMIS(metal-ferroelectric-metal-insulator-semiconductor) FET devices.[4,5,6] Most of ferroelectric memory devices which have been studied and developed used the ferroelectric thin films as a charge storage capacitor with MFM structure. Also, the MFS and MFMIS FET devices have been studied for memory devices and applied to an adaptive learning applications using partial switching characteristics of ferrolectric thin films.[7]

In this study, PZT thin films were fabricated by sol-gel method introduced by Budd et al.[8] The platinized silicon dioxide/silicon wafers were used as a substrate. Finally we made MFM capacitors which have Pt/PZT/Pt/SiO2/Si structure. Then, we measured the switching current curves of PZT thin films with a variation of the Zr/Ti mol% and applied voltages, and discussed the results. Also, we investigated the switching characteristics of fatigued PZT thin films and the partial switching characteristics.

2. Experiment

(1) Sample preparation

PZT(Zr/Ti=80/20, 60/40, 50/50, 40/60, and 20/80) coating solutions were prepared by the conventional sol-gel processing propose by Budd, et al.[8] and were deposited on Pt/SiO2/Si substrate by spin coating method. The coating solution were prepared from lead acetate, titanium iso-propoxide, and zirconium n-propoxide precursors. The films were dried at 120℃ for 10 minutes and 400℃ for 10 minutes and finally annealed at 500℃~800℃ for 30 minutes in the air. Figure 1 shows the X-ray diffraction of the PZT thin films according to the Zr/Ti mol% and sintering temperature. As shown in Figure 1 (a) the perovskite structure is shown at the temperature above 600℃, but the pyrochlore phase is shown at the temperature 800℃. The PZT films annealed at 650℃ and 700℃ exhibit every perovskite orientation of PZT ceramics and no pyrochlore phase. Variation of the lattice constant and structure of PZT thin films according to the Zr/Ti mol% is shown in Figure 2[9]. For electrical measurement, platinum top electrode was deposited by sputtering method. The thickness of PZT thin films was about 400 nm and radius of top electrode was 30μm.

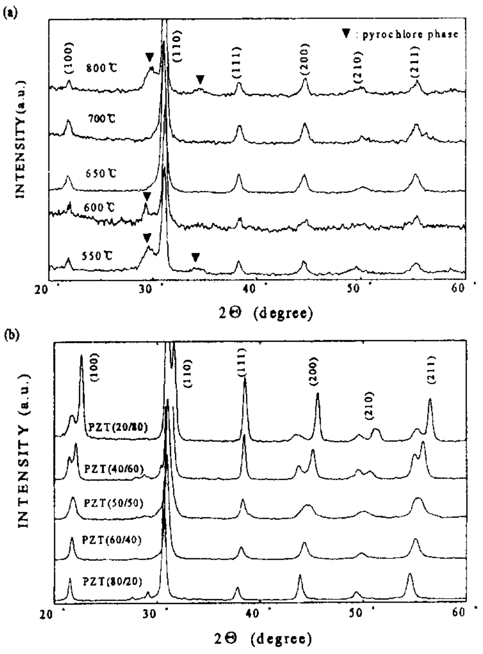

Figure 1. X-ray diffraction pattern of the PZT thin films according to(a) sintering temperature, and (b) Zr/Ti mol %.

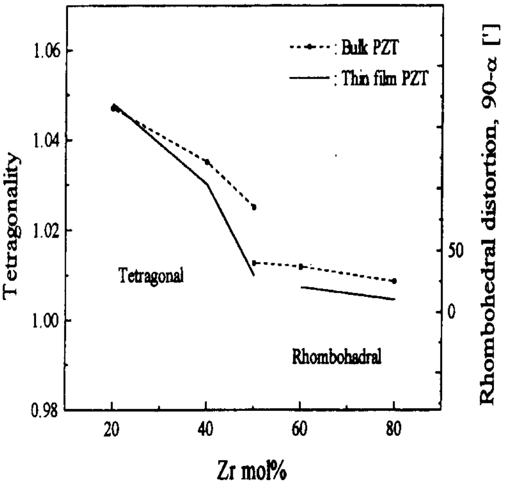

Figure 2. The variation of the crystal structure according to the Zr/Ti mol% of bulk and thin film PZT ceramics[9].

(2) Measuring electrical properties

The dielectric constant and loss were measured at 1kHz. Hysteresis measurement was carried out by the conventional Sawyer-Tower circuit using 1kHz sinusoidal wave. Signal forms of applied pulses for polarization switching and switching current measurement circuit are shown in Fig. 3. Signal forms in Figure 3 (b) is for the full switching curves and (c) is for the partial switching curves of the PZT thin films.In case of the input pulses for full switching curves in Fig. 3(b), there are two same square + and − pulses. The first + square pulse of them were named SP which is for the switching curves of − polarized PZT thin films and the second + square pulse(NP) is for the nonswitching curves of the + polarized PZT thin films. The pulse SM which is followed by the pulse NP is for the switching curves of the + polarized PZT thin films and the second − square pulse(NM) is for the nonswitching pulse of the − polarized PZT thin films. In order to investigate the switching characteristics according the amplitude of the SP and NP pulses, the amplitude of the pulse, Vm, was varied from 4 to 14 volts. Figure 3 (c) shows the input signal for the partial switching characteristics. The PS pulse in Figure 3 (c) which have −5 volts and 50 nano second width was applied to polarize the PZT thin films partially and the SP pulse was applied for partial switching curves. The amplitude of the SP in Figure 3 (c) was 10 volts. To investigate the partial switching characteristics of the PZT thin films, the number of the applied pulses of PS was increased form 1 to 10. Figure 3 (d) shows the signals for fatigueing PZT thin films. Figure 4 shows the switching and non switching current curves. The switching time(ts) was defined as the time it takes for the current transient to decay to 10% of its maximum value that was defined as Imax[10,11].

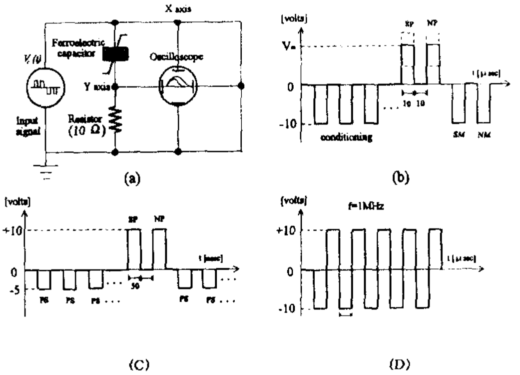

Figure 3. Input signal and test circuit for polarization switching current curve. (a) test circuit, (b) input signal for full switching, (c) input signal for partial switching, and (d) input signal for fatigue.

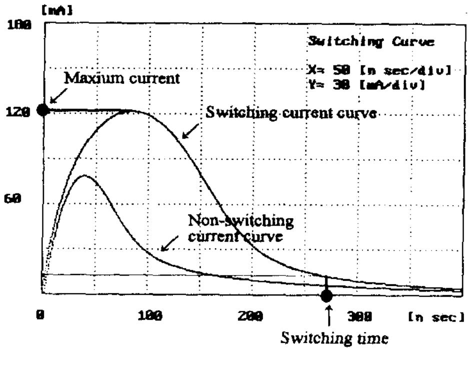

Figure 4. Ferroelectric polarization switching curves and the definition of switching time(ts) and Imax.

For the purpose of measuring the switching characteristics of fatigued specimen, the signal in Figure 3 (d) was applied to the PZT thin films up to 10_{10} cycles and the frequency and amplitude of the pulse were 1MHz and ±10 volts respectively.

3. Results & Discussion

As a results of the X-ray diffraction pattern and analysis in Figure 1 and 2, it was also found that the microstructural characteristics of PZT thin films which are fabricated by sol-gel process in this experiment were very similar to those of bulk ceramics.[9] Also, we measured the dielectric and hysteresis characteristics of PZT thin films according to the Zr/Ti mol%. As shown in Figure 5 (a) and (b), the dielectric constants were from 275 to 745 and dielectric losses were from 0.016 to 0.03, and remament polarizations were from 12 to 32 μC/㎠ and coercive fields were from 52 to 181 kV/cm. Then, polarization switching curves were measured with a variations of the Zr/Ti mol% of PZT thin films. To obtain the full switching curves, we applied ±10 volts double bipolar square pulses as shown in Figure 3(b). Figure 6 shows the full polarization switching and non-switching curves of PZT(60/40) and (40/60) thin films. There are two curves in each of PZT(40/60) and PZT(60/40) thin films. One of them is switching(SW) and another is non-switching(NS) curve. SW and NS curves were measured by the SP and NP pulses of the input signal shown in Figure 3(b), respectively. Also, Figure 7 shows the variation of ts and Imax versus Zr/Ti mol% of PZT thin films. In Figure 7, the switching times(ts) were found to be increased as the Zr mol% decreased. Also, the Imax were varied according to Zr/Ti mol% of PZT thin films, but the tendency of Imax with the variation of Zr/Ti mol% was different from that of ts. In case of ts, they were decreased as the Zr/Ti mol% increased. Imax was found to have largest value at Zr 50 mol%.

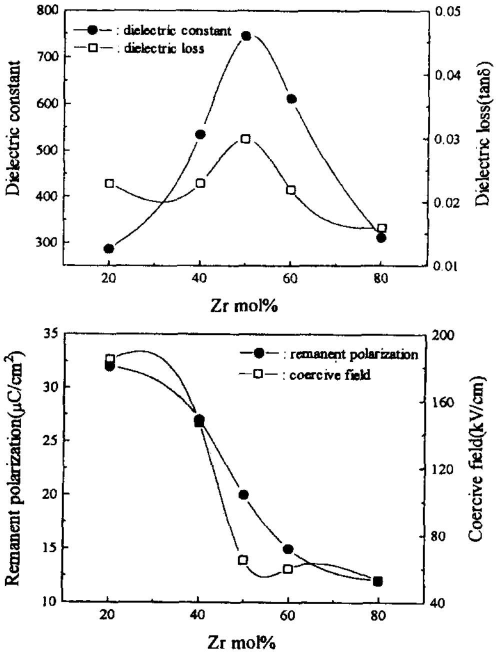

Figure 5. The variation of the (a) dielectric constant, and (b) remanent polarization and coercive field versus Zr/Ti mol% of PZT thin films

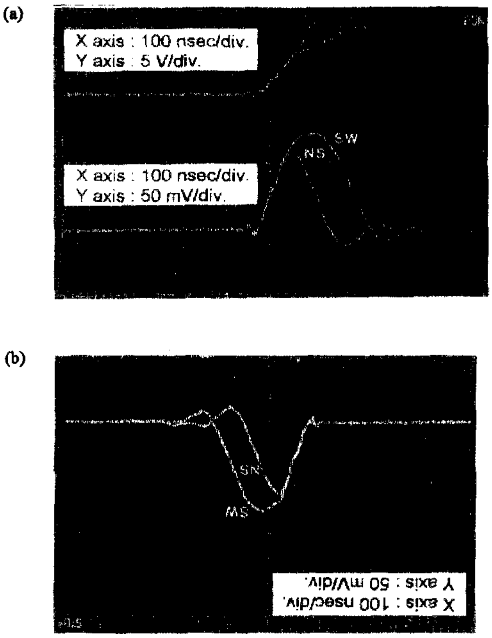

Figure 6. Polarization switching curves of PZT thin films. (a) PZT(60/40), and (b) PZT(40/60).

This Imax curve was very similar to the dielectric constant curve shown in Figure 5 (a). Comparing with these two graphs, the Imax was more dependent upon the dielectric constant than remanent polarization or coercive field. In the

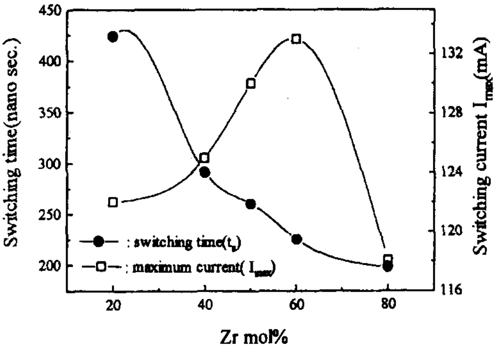

Figure 7. The variations of the ts and Imax versus Zr/Ti mol % of PZT thin films.

point of view of lattice modeling of ferroelectric polarization switching, Imax also depend on the remanent polarization[12]. As it is well known that the switching current transient of ferroelectric materials are occurred in two parts. One is linear dielectric component and the other is nonlinear dielectric component. The current occurred by a linear dielectric component is expressed by a simple exponential function as follow.

$$i(t)_{linear} = I_0 e^{-t/\tau} \qquad (1),$$

where $\tau = RC$ and is called time constant. This imply that the switching current curve of the PZT thin films include the linear dielectric component of PZT thin film and also Imax should depend on the dielectric constant which is a linear dielectric component. The switching current occurred by nonlinear dielectric component is due to the switching of dipole polarization in ferroelectric materials. In case of switching current by the dipole polarization, the switching time(ts) and maximum current(Imax) is determined by the hysteresis characteristics of the ferroelectric materials. Also, the switching mechanism of the PZT ceramics is not simple like equation (1), so ts should be longer and Imax should be smaller than those of switching curve of linear dielectric component. As a result of the above experiment, ts and Imax were strongly dependent upon the hysteresis characteristics such as remanent polarization and coercive field and also dielectric constant of PZT thin films.

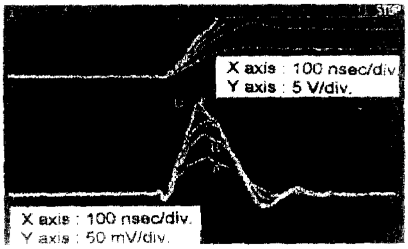

Figure 8. Changes of ts and Imax according to the applied voltages. (A:4 volts, B:8 volts, C:10 volts, D:12 volts, and E:14 volts).

width of the applied pulses, the polarization switching curves were measured. We got partial

To investigate the polarization switching current according to the variation of the applied voltages, we varied the amplitude of applied pulses SP and NP, which are shown in Figure 3(b), from 4 to 14 volts. The result is shown in Figure 8 and it was found that the ts was decreased and Imax was increased as the amplitude of SP increased. This result was similar to the result of paper reported by P. K. Larsen et al. [11]and Tokumitsu et al..[13] The switching time is depend on the electric field E and its proportionality was determined by following equations[11,14,15].

$$t_s = 1/(E - E'')^x$$
$$(x = 1 \sim 1.4) \text{ or } \exp(\alpha/E), \qquad (2),$$

where, E'' and α are threshold and activation field, respectively.

The ferroelectric thin films can be used as a gate oxide material for MFS or MFMIS FET devices. Also, the devices is applicable to the analog-memory weights devices for adaptive learning neuron circuit. In this case, the polarization state of the ferroelectric gate oxide will be determined by the number or density of applied signals to the gate ferroelectric thin films of the devices. This kind of switching mechanism was called partial switching. In order to investigate the polarization state of the PZT thin films after a certain number of the applied pulses which is PS pulse in Figure 3(c), the pulses with 5 volts and 50 nsec width were applied to the MFM PZT capacitors. As shown in Figure 3(c), we controlled the number of input pulse PS to get different polarization state in MFM PZT capacitors. According to the total switching curves according to the number of input PS pulses at the SP pulse of the input signal in Figure 8. As the Figure 9 shows, the ts and Imax were decreased as the total width of the applied pulses increased from 50 nano seconds to 500 nano seconds. This results indicate that the

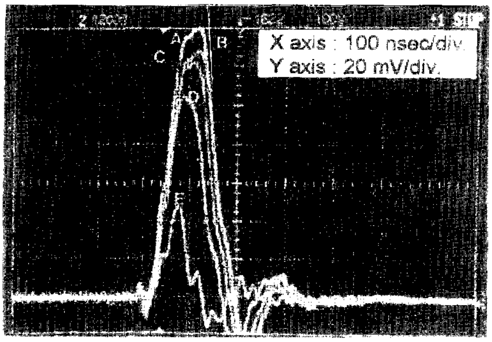

Figure 9. The switching current curves according to the total width of the applied pulses.(A:50 nsec, B:100 nsec, C:150nsec, D:200 nsec, and E:500 nsec).

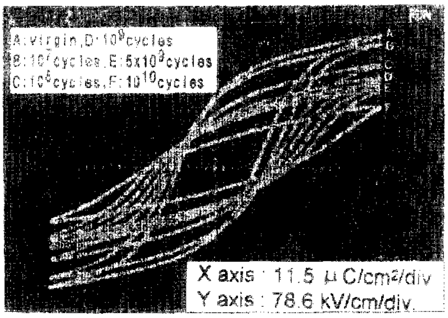

Figure 10. Hysteresis curves of the PZT(40/60) thin films according to the cumulative switching cycles.(A:virgin, B:10_7 cycles, C:10_8 cycles, D:10_9, E:5x:10_9 cycles and F:10_{10} cycles).

polarization state of PZT thin films can be controlled by applying relatively small amplitude and short period pulses. Also, the current(IDS) from the drain to source of the MFS or MFMIS FET devices will be determined by the polarization state of the gate ferroelectric thin films. Therefore, the devices can be used as a adaptive learning neuron circuits.

One of the most important problem of the PZT thin film for memory applications is the fatigue which is characterized by the decrease of the remanent polarization and increase of the coercive field after continuous polarization switching cycles.

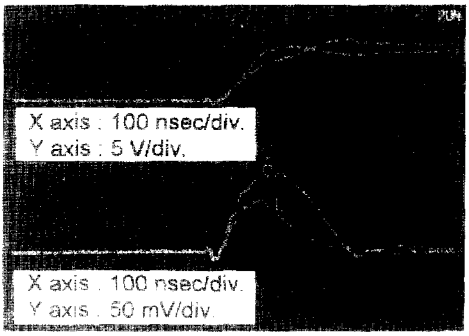

Figure 11. Polarization switching curves of the PZT(40/60) thin films before and after fatigue.(A:virgin, and B:fatigued(after 10_{10} cycles)).

Many reports have been published to investigate and verify the fatigue mechanism of PZT thin films after continuous polarization switching cycles.[16,17,18] In order to investigate the switching characteristics of fatigued PZT thin films, we applied 10_{10} cycles 10 volts bipolar rectangular pulses to the MFM PZT capacitors. Figure 10 shows the hysteresis curves of PZT(40/60) thin films according to the cumulative polarization switching cycles. As shown in Figure 10, remanent polarization and coercive field of fatigued PZT thin film were decreased to 1/3 and increased to 5/3 of its virgin state, respectively. Polarization switching curves of these virgin and fatigued specimen of the PZT thin films were shown in Figure 11. The ts and Imax of the fatigued specimen were shorter and smaller than virgin ones. This is due to variation of the remanent polarization and coercive field.

4. Conclusion

In this paper, we have studied switching characteristics of ferroelectric PZT thin films prepared by sol-gel processing. As a result of the measurement of the dielectric and hysteresis characteristics of PZT thin films, they were very close to the those of the bulk PZT ceramics. Also, It was found that the ts and Imax were dependent upon the dielectric constant and remanent polarization and coercive field, respectively. When the applied voltage was increased, the switching time and Imax were decreased and increased, respectively. Also, we found that the polarization state of the PZT thin films could be controlled by the width and amplitude of the applying pulses. The ts and Imax were decreased as the width of the applied pules were increased. As a result of this experiment, the MFS or MFMIS FET devices using PZT thin films will be applicable to the adaptive learning neuron circuits. In case of fatigued specimens, it was demonstrated that the ts and Imax were decreased compared with virgin specimens.

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