ELECTRICAL CHARACTERISTICS OF SOL-GEL DERIVED Pb(Zr,Ti)O₃ THIN FILMS

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Abstract

The fatigue of both hysteresis loop and dielectric constant (ε) of sol-gel derived Pb(Zr₀·₅₃,Ti₀·₄₇)O₃ thin films was investigated. Both ε and remanent polarization (P_r) decreased with switching cycles. The growth of the low-ε interface layer with switching cycles was shown by measuring thickness dependence of ε at several switching cycles. The decrease of ε and P_r is mainly due to this growth of the low-ε interface layer.

1. Introduction

Recently, Pb(Zr,Ti)O₃ (PZT) thin films have been widely investigated for their applications in non-volatile random-access memory (NVRAM). For NVRAM application, P_r must be stable because P_r is directly related to the effective read-out voltage. However, it has been reported for PZT thin films that P_r decreases with the increase of number of polarization reversals.¹-³ This polarization degradation is generally called fatigue. Several fatigue mechanisms have been proposed.⁴-⁶ They can be divided into two groups: ferroelectric-electrode interface effects and ferroelectric bulk cause. Since it is difficult to separate interface and bulk effects, which effects is dominant on fatigue is not yet clarified.

In this study, the fatigue of both hysteresis loop and ε of sol-gel derived PZT thin films was investigated. The model which assumes the existence of a low-ε interface layer between the ferroelectric layer and the electrode was examined by measuring thickness dependence of ε at several switching cycles. Furthermore, the applied voltage dependence of P-E hysteresis loop of the fatigued sample was compared with that of the initial sample.

2. Experimental

PZT(Zr/Ti=53/47) thin films were synthesized on Pt/Ti/SiO₂/Si substrates using a sol-gel process. Details of this procedure were given elsewhere.⁷ The obtained film thicknesses were 127, 202 and 305nm.

For electrical property measurements, gold was deposited on the PZT films as top electrodes. The dot size was 0.09mm². For the fatigue test, the 100kHz square wave was applied to the films. The electric field was set to be the same (2.5V/100nm) for each film, i.e. 3.2V for the 127nm-thick film, 5V for the 202nm-thick film, and 7.5V for the 302nm-thick film. P_r and E_c were measured using a Sawyer-Tower circuit with a sinusoidal wave of 100 Hz. Capacitance was measured without bias voltage at 10 kHz after applying the positive voltage to observe dielectric property in the same polarization condition.
3. Results and Discussion

Figure 1 shows the fatigue characteristics of $P_r$. All the films showed considerable decrease of $P_r$ before $10^9$ cycles. Figure 2 shows the fatigue characteristics of $\varepsilon$. Dielectric constant also decreases with switching cycles.

To understand the dependence of $\varepsilon$ on thickness and switching cycles, we assume that a low- $\varepsilon$ layer exists adjacent to the electrode and that the remaining part has a high $\varepsilon$. In this model, the equivalent circuit of the PZT film is a series of a capacitor of the low- $\varepsilon$ layer and a capacitor of the high- $\varepsilon$ layer as shown in Fig.3. Hence, the measured capacitance ($C_{\text{meas}}$) is related to the capacitance of the low- $\varepsilon$ layer ($C_{\text{low}}$) and that of the high- $\varepsilon$ layer ($C_{\text{high}}$) as follows:

$$\frac{1}{C_{\text{meas}}} = \frac{1}{C_{\text{high}}} + \frac{1}{C_{\text{low}}}$$

$$\frac{1}{C_{\text{meas}}} = \frac{d_{\text{high}}}{\varepsilon_0 \varepsilon_{\text{high}} A} + \frac{d_{\text{low}}}{\varepsilon_0 \varepsilon_{\text{low}} A}$$

$$\frac{1}{C_{\text{meas}}} = \frac{1}{\varepsilon_0 A} \left( \frac{1}{\varepsilon_{\text{low}}} - \frac{1}{\varepsilon_{\text{high}}} \right)$$

where $d_{\text{high}}$ and $\varepsilon_{\text{high}}$ are thickness and dielectric constant of the high- $\varepsilon$ layer,
Fig. 6 Applied voltage dependence of $P_{r}$ and $P_{\text{max}}$.

respectively; $d_{\text{low}}$ and $\epsilon_{\text{low}}$ are those of the low- $\epsilon$ layer; $A$ is the electrode area and $\epsilon_{0}$ the dielectric constant of free space. If the second term of the right side of eq.(1) is independent of the thickness, the reciprocal of the measured capacitance ($1/C_{\text{meas}}$) should have linear dependence on the thickness ($d$). $1/C_{\text{meas}}$ at several fatigue cycles is plotted against the film thickness in Fig. 4. $1/C_{\text{meas}}$ at the same fatigue cycles are on one line except for that at $10^9$ cycles. This result indicates that $d_{\text{low}}/\epsilon_{\text{low}}$ of films of different thickness is almost the same at the same fatigue cycles. From the slope of the $1/C_{\text{meas}}$ line, $\epsilon_{\text{high}}$ is calculated to be around 1400. Furthermore, assuming $\epsilon_{\text{high}} \gg \epsilon_{\text{low}}$, $d_{\text{low}}/\epsilon_{\text{low}}$ can be calculated from the y-intercept of the $1/C_{\text{meas}}$ line. The calculated value of $d_{\text{low}}/\epsilon_{\text{low}}$ is plotted in Fig. 5. This result shows that the low- $\epsilon$ interface layer grows with switching cycles.

To understand the effect of the low- $\epsilon$ interface layer, the applied voltage dependence of P-E hysteresis loop was measured before and after switching cycles. Figure 6 shows the applied voltage dependence of $P_{r}$ and $P_{\text{max}}$ of the 127nm-thick film at initial condition and after $10^9$ switching cycles. At initial condition $P_{r}$ saturates around 8V, though after switching cycles $P_{r}$ does not saturate even at 11V. Hence, higher voltage is necessary to polarize the fatigued sample. To apply further voltage was unable because the sample broke down at 12V. When there is a low- $\epsilon$ interface layer, the voltage applied to the inner ferroelectric layer ($V_{f}$) is expressed as follows:

$$V_{f} = \frac{C_{\text{low}}}{C_{\text{high}} + C_{\text{low}}} V_{\text{meas}}$$

$$= \frac{1}{1 + \frac{C_{\text{high}}}{C_{\text{low}}}} V_{\text{meas}}$$

$$= \frac{1}{1 + \frac{d_{\text{low}} \epsilon_{\text{high}}}{d_{\text{high}} \epsilon_{\text{low}}}} V_{\text{meas}}$$

where $V_{\text{meas}}$ is the measured applied voltage. $d_{\text{low}}/\epsilon_{\text{low}}$ of the initial sample was estimated to be 0.058nm, while that of the fatigued was estimated to be 0.12nm. On the other hand, $d_{\text{high}}$ and $\epsilon_{\text{high}}$ are 120nm and 1400, respectively. Thus, $V_{f}$ of the initial and that of the fatigued are 60$\%$ and 42$\%$ of the measured applied voltage, respectively. Figure 7 is the replotted data of $P_{r}$ and $P_{\text{max}}$ against $V_{f}$. The curve of $P_{r}$ agrees well
with each other, while there is difference between those of $P_{\text{max}}$. The mechanism of $P_{\text{max}}$ degradation needs further investigation.

To clarify what causes the growth of the low- $\varepsilon$ interface layer, +5V square pulse was applied to the 191nm-thick film, and $P_r$ and $\varepsilon$ were measured. Thus this sample was subject to the applying voltage without polarization reversals. The results are plotted in Fig.8. Neither degradation of $P_r$ nor $\varepsilon$ was observed. Hence, the growth of the low- $\varepsilon$ interface layer was caused by the polarization reversals, not simply by applying voltage.

4. Conclusions

The fatigue of both hysteresis loop and $\varepsilon$ of sol-gel derived Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ thin films was investigated. The decrease of $\varepsilon$ and $P_r$ with switching cycles was explained by the model in which the low- $\varepsilon$ interface layer grows with switching cycles. The change of the applied voltage dependence of $P_r$ with switching cycles also supported this model.

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References