

# Polarization Switching Behavior of HfO<sub>2</sub>-based Ferroelectric Ultrathin Films Studied through Coercive Field Characteristics

Shinji Migita<sup>1</sup>, Hiroyuki Ota<sup>1</sup>, Hiroyuki Yamada<sup>1</sup>, Keisuke Shibuya<sup>1</sup>, Akihito Sawa<sup>1</sup>, and Akira Toriumi<sup>2</sup>

<sup>1</sup>AIST and <sup>2</sup>The Univ. of Tokyo  
Central 2, Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan  
E-mail: s-migita@aist.go.jp

## Abstract

**Polarization switching behavior of HfO<sub>2</sub>-based ferroelectric ultrathin films is investigated through the examination of remnant polarization (*Pr*) and coercive field (*Ec*). The *Ec* values are always as large as 1 MV/cm and little affected by the chemical composition and film thickness, while the *Pr* values changed with these parameters largely. Ferroelectric domain in nanometer-scale seems to be the key to understand this phenomenon.**

## 1. Introduction

The polarization switching in ferroelectric capacitors progresses through the nucleation and growth of reversed domains (Fig. 1). Experiments of many ferroelectric capacitors show that the electric field for the switching depends on the film thickness, and the relationship between the coercive field *Ec* and the thickness *d* can be expressed as follows [1]:

$$Ec \sim d^{2/3} \quad (1)$$

Experimental results of many ferroelectric materials PZT [2], SrBiTaO [3], BaTiO [4], and BiTiO [5] show that this trend is appropriate for more than two orders of thickness range (Fig. 2). In this work, we examined the ferroelectric properties of ultrathin Hf-Zr-O films and discuss about the unique switching behavior.

## 2. Experiment

Metal/ferroelectric/metal capacitors were prepared on heavily doped Si substrates by the sputtering technique. Metal electrodes were TaN. Hf-Zr-O films were prepared by the co-sputtering of HfO<sub>2</sub> and ZrO<sub>2</sub> targets. Chemical compositions were adjusted by frequent shuttering of two targets. Crystallization anneal was performed at between 600 and 700 °C for 1 min in a vacuum condition. The capacitors were fabricated by lithography and dry etching.

## 3. Results and Discussion

In-plane XRD pattern shows that the crystallization is progressing by the annealing at 600°C (Fig. 3). Indices of diffraction peaks tell that the film consists of several phases, at least orthorhombic and monoclinic phases. Cross-sectional TEM images show that crystallization is completed in both thin and thick films. Film thickness is uniform and the interfaces with TaN electrodes are flat. Contrasts of crystal grains in indicate that Hf-Zr-O crystals have columnar shapes whose heights are identical with the film thickness. Thus it is speculated that some of these crystal grains have orthorhombic structure and show ferroelectricity. *P-V* curves of a 10-nm-thick Hf-Zr-O film show a well-defined ferroelectric behavior (Fig. 5).

The impacts of chemical composition and film thickness on ferroelectricity were examined. Irrespective of the variation of these parameters, ferroelectric behavior was confirmed by *P-V* measurements (Figs. 6 and 7). Summaries of the *Ec* and the remnant polarization *Pr* are shown in Fig. 8. The large dependence of *Pr* values with these parameters infers that the volume fraction of ferroelectric phase in the film is changing. It is guided that 50% of Zr composition and film thickness about 10 nm is a good design for the enhancement of polarization. In contrast, the *Ec* values are always around 1 MV/cm and insensitive with these parameters. In order to highlight this feature, the *Ec* values with film thickness are plotted in Fig. 2, together with the experimental reports of Hf-Zr-O [6] and Y-HfO<sub>2</sub> [7]. It is clear that the *Ec* values of HfO<sub>2</sub>-based ferroelectric capacitors do not show the thickness dependence. Although further experiment is still needed to clarify the mechanism, at present we speculate the reason as follows (Fig. 9). The HfO<sub>2</sub>-based film is not a single phase, but the ferroelectric grains are dispersed in the dielectric phase. The large *Ec*~1 MV/cm tells that the grain size of ferroelectric phase is smaller than the critical nucleus of domain switching (*v<sub>cr</sub>* in Fig. 1). In addition, the thickness dependence of *Pr* in Fig. 8(b) shows that the size or the number of ferroelectric grains is reducing with the increment of thickness. Thus ferroelectricity of HfO<sub>2</sub>-based films is governed by a nanometer-scale region in the film.

## 4. Conclusions

Ferroelectric properties of HfO<sub>2</sub>-based films cannot be evaluated by the measure of conventional ferroelectric materials. The unique character seems to be yielded by the composite of ferroelectric and dielectric grains mixed in the nanometer-scale. This understanding will be helpful to integrate this material into advanced electron devices such as FeRAM and FE-FETs.

## Acknowledgement

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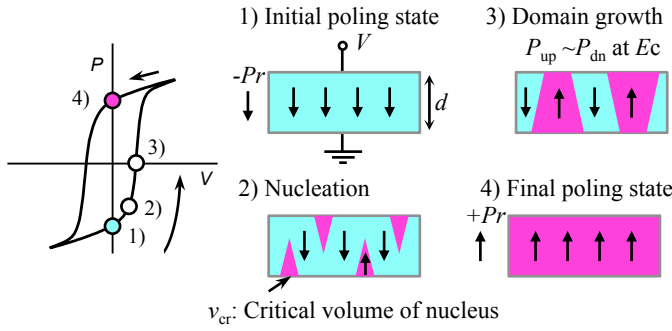


Fig. 1. Schematic of polarization switching behavior in ferroelectric films. Starting from the 1) initial poling state, 2) reversed nuclei are formed when the electric field is large enough to stabilize the critical nuclei. 3) Coercive field is defined at the voltage when the total poling amount is zero. 4) The switching is completed.

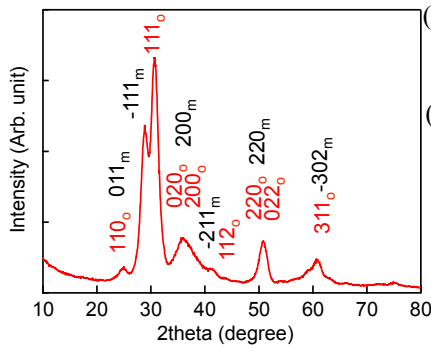


Fig. 3. In-plane XRD pattern of 10-nm-thick  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  film on TaN electrode annealed at 600°C.

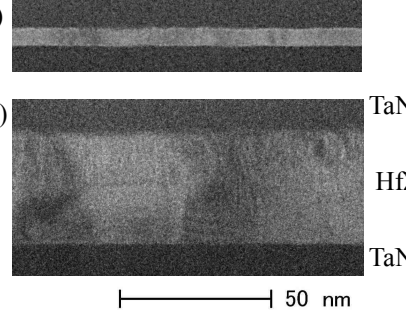


Fig. 4. Cross sectional TEM images of  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  films sandwiched in TaN electrodes and annealed at 600°C. (a) 6.8 nm and (b) 41 nm.

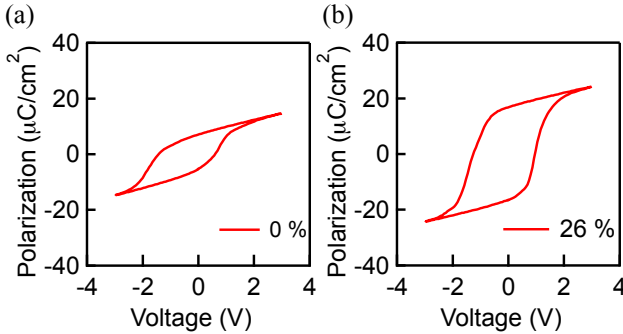


Fig. 6. P-V characteristics of 10-nm-thick Hf-Zr-O films with different Zr composition,  $\text{Zr}/(\text{Zr} + \text{Hf})$ .

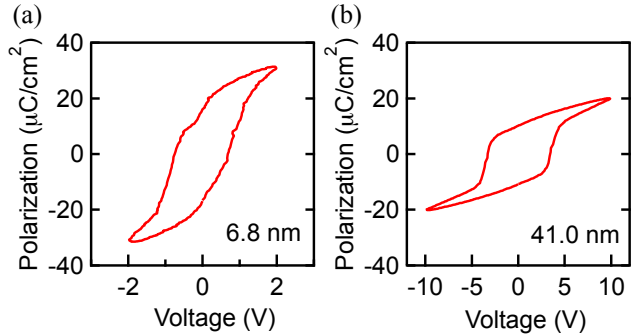


Fig. 7. P-V characteristics of thin and thick  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  films.

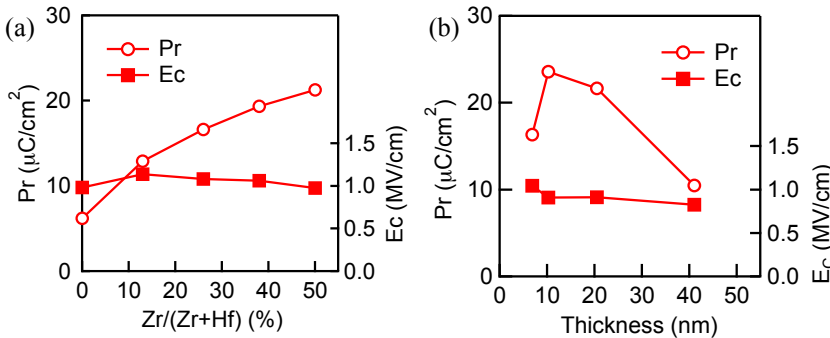


Fig. 8. Dependences of  $P_r$  and  $E_c$  values on (1) metal composition and (b) film thickness.

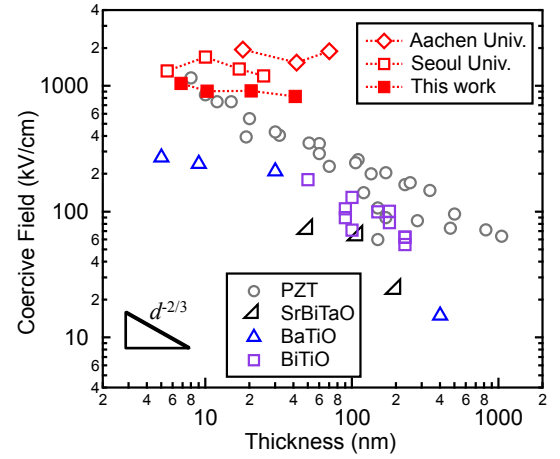


Fig. 2. Experimental results of thickness dependences of ferroelectric coercive fields.

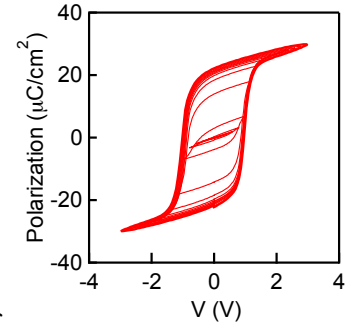


Fig. 5. P-V characteristics of 10-nm-thick  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  film annealed at 700°C.

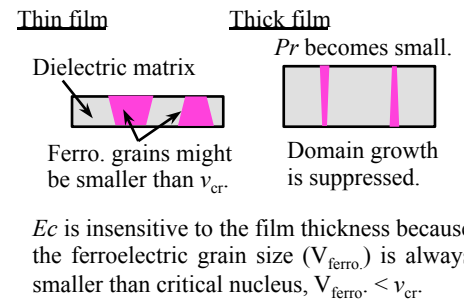


Fig. 9. Model of the switching behavior of  $\text{HfO}_2$ -based ferroelectric films.