# Thickness-dependent ferroelectric phase evolution in doped HfO<sub>2</sub>

Lun Xu<sup>1\*</sup>, Tomonori Nishimura<sup>1</sup>, Shigehisa Shibayama<sup>1</sup>, Takeaki Yajima<sup>1</sup>, Shinji Migita<sup>2</sup>,

and Akira Toriumi<sup>1</sup>

<sup>1</sup> Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan

<sup>2</sup> National Institute of Advanced Industrial Science & Technology (AIST), Tsukuba, 305-8569, Japan

\*Phone: +81-3-5841-1907, E-mail: xulun@adam.t.u-tokyo.ac.jp

Abstract: We discussed thickness-dependent ferroelectric phase evolution in doped HfO<sub>2</sub> films. Dopant (Ge) incorporation can drive the M-O-Tphase transition, but is not the only factor for ferroelectric O phase stabilization. Ferroelectric Ophase seems an intermediate phase, which can reduce the nucleation energy of M phase in T-Mphase transition. From a kinetic viewpoint, we suggest that the larger M phase nucleation energy in the thinner film is better for ferroelectric O phase stabilization.

## 1. Background and objectives

Recently, ferroelectric  $HfO_2$  has attracted a lot of interests due to attractive applications in nonvolatile memories, ferroelectric FETs, and negative capacitance FETs (NCFETs).<sup>1, 2</sup> For driving the ferroelectricity in  $HfO_2$ , several methods have been reported, such as dopant incorporation, capping layer confinement, film thickness scaling down, and crystallization process control.<sup>1</sup> However, the ferroelectric orthorhombic (*O*) phase stabilization process is still not well understood. This paper reports the ferroelectric *O* phase evolution process, and discusses key factors for stabilizing ferroelectric *O* phase.

## 2. Experimental

Different thick Ge-doped HfO<sub>2</sub> films were prepared by sputtering on highly doped p-type Ge (111) after the methanol, diluted HCl and HF solution cleaning. The dopant atomic percentage (dop%) was calibrated by the X-ray photoelectron spectroscopy (XPS). Top Au electrode ( $5.7 \times 10^{-5}$  cm<sup>2</sup>) was thermally evaporated on each doped HfO<sub>2</sub> film after the post deposition annealing (PDA) at 600°C in 1-atm N<sub>2</sub> for 30 s. GIXRD and P–E (10 kHz) measurements were carried out to characterize the film properties.

## 3. Dopant-induced HfO<sub>2</sub> ferroelectricity

The GIXRD patterns and P–E characteristics of 18nm-thick  $HfO_2$  films with 0, 1.92, 3.67, and 4.58% Ge concentrations are shown in **Figs. 1(a)-(d)**, respectively. It is noticed that Ge doping can stabilize highly symmetric  $HfO_2$  phases (orthorhombic/tetragonal/cubic: O/T/C). Moreover, the ferroelectricity is considerably enhanced by 3.67% Ge doping, but is strongly suppressed by 4.58% Ge doping. For Ge doping, the shorter Ge-O (compared with Hf-O) bonding favors the tetragonal structure.<sup>3</sup> Since the energy difference between tetragonal and ferroelectric O phases is estimated to be very small,<sup>4</sup> it is expected that the structural transition from T to ferroelectric O phase may probably be driven by an electric field. Therefore, the observed anti-ferroelectric P–E hysteresis of 4.58% Ge-doped HfO<sub>2</sub> is possibly owing to the reversible T-O phase transition under an electric field.



**Fig. 1 (a)-(d)** XRD patterns and P–E hysteresis (10 kHz) of 18 ( $\pm$ 1) nm HfO<sub>2</sub> films with 0, 1.92, 3.67, and 4.58% Ge doping concentrations, respectively.

### 4. Thickness-dependent HfO<sub>2</sub> ferroelectricity

Next. thickness-dependent ferroelectricity of Ge-doped HfO<sub>2</sub> is discussed. P-E curves of 18, 28, 62, and 250 nm thick Ge-doped HfO<sub>2</sub> films are shown in Fig. 2(a). Here, we carefully checked the doping concentration-dependent ferroelecectricity for each thickness. The P-E curves in Fig. 2(a) reprensent the strongest ferroelectricity for each thickness. The swithcable polarization  $(Psw=Pr^+-Pr^-)$  and coersive filed (Ec) are summarized as a funtion of the film thickness in the Figs. 2(b) and (c), respectively. In the polycrystalline HfO<sub>2</sub>, the P-E hysteresis shape will be deformed by including paraelectric phases. For example, M phase will lead to a dumpy P-E loop,

while T/C phase will lead to a slender one. Therefore, we extracted Ec values from transient curent versus electric field (I-E) curves. With the increase of film thickness, both *Psw* and *Ec* are decreased. The average grain size, shown in Fig. 2(d), was estimated by using the classical Scherrer's formula,  $D=0.9\lambda/\beta cos\theta$ , where  $\lambda$ ,  $\beta$  and  $\theta$  are the X-ray wavelength, the corrected half-width at half intensity of monoclinic (M) (-111) and (111) peaks, and the diffraction peak angle, respectively. In the thinner region (<30nm), the decrease of grain size might be responsible for the increased Psw, which is due to the larger contribution from the surface energy.<sup>5</sup> However, for the thicker region (>30nm), the grain size is not increased, indicating other effects may be responsible for the decrease of Psw.



**Fig. 2 (a)** P–E hysteresis (10 kHz) of 18, 28, 62 and 250 nm thick Ge-doped HfO<sub>2</sub> films, (**b**)  $P_{SW}$ , (**c**) 2*Ec* and (**d**) grain sizes are shown as a function of HfO<sub>2</sub> thickness.

For more clearly understanding the ferroelectric phase evolution in different thick HfO<sub>2</sub> films, the phase composition diagram is shown in **Fig. 3**, in which  $P_{SW}$ is shown as a function of  $r_M$ . The M phase fraction  $(r_M)$ estimated according was to the formula.  $r_M = [I_{M(-111)} + I_{M(111)}] / [I_{M(-111)} + I_{M(111)} + I_{O/T/C(111)}]$ , in which I is the integrated peak intensity in GIXRD patterns. Here, Ge incorporation was used to drive the phase evolution from M to T phase in HfO<sub>2</sub>. The ferroelectric O phase, shown in Fig. 3, becomes harder to be stabilized in the thicker films, indicating that Ge incorporation is not the sufficient condition for ferroelectric O phase stabilization. Moreover, it is also noted that the surface energy effect is not dominant because of the comparable grain sizes in 18, 28, 62, and 250 nm thick HfO<sub>2</sub> films.

As shown in Fig.3, for maximum Psw points, both M and T phases coexist. Therefore, it is inferred that ferroelectric O phase stabilization is more related to the kinetic process of T-M transition. Unlike the T-M

phase transition, which is accompanied by a large volume expansion ( $\Delta V \sim 5.9\%$ ) and shape strain (dominated by a shear stain,  $\gamma \sim 0.15$ ), the volume increase ( $\Delta V \sim 2.0\%$ ) and shape strain (dominated by a dilatational strain,  $\xi \sim 0.02$ ) are much smaller for the T-O phase transition.<sup>6</sup> Therefore, the formation of intermediate ferroelectric *O* phase might effectively reduce the nucleation energy of *M* phase. From a kinetic viewpoint, the larger *M* phase nucleation energy, possibly from the defect effect or strain effect, might be responsible for ferroelectric *O* phase stabilization in the thinner film.



**Fig. 3** Phase composition diagram for 18, 28, 62, and 250 nm Ge-doped HfO<sub>2</sub> films, in which  $P_{SW}$  is shown as a function of *M* phase fraction.

#### 5. Conclusions

We discussed the ferroelectric O phase evolution in different thick HfO<sub>2</sub> films. Ferroelectric O phase favors to be formed in the thinner film, which is not only due to the dopant effect and grain size effect. We suggest that ferroelectric O phase formation is more related to the T-O-M transition process. The larger M phase nucleation energy in thinner film might provide a better opportunity for ferroelectric O phase stabilization.

## Acknowledgement

This work was supported by JST-CREST. Grant Numbers JPMJCR14F2, Japan.

#### References

- [1] M. H. Park, et al., Adv. Mater. 27, 1811 (2015).
- [2] S. Salahuddin, et al., Nano Lett. 8, 405 (2008).
- [3] C. K. Lee, et al., Phys. Rev. B 78 012102 (2008).
- [4] S. E. Reyes-Lillo, et al., Phys. Rev. B **90**, 140103 (2014).
- [5]S. V. Ushakov, et al., Phys. Stat. Sol. (b) **241(10)**, 2268 (2004).
- [6] P. M. Kelly, et al., Progress in Materials Science **47**, 463 (2002).