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# Understanding the formation of the metastable ferroelectric phase in hafnia-zirconia solid solution thin films

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#### Activation energy estimation from experiment

The Johnson-Mehl-Avrami (JMA) model is a standard method to analyze the phase transformation.<sup>[S1-S3]</sup> However, the orthorhombic or tetragonal to monoclinic phase transformation in the extremely thin Hf<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> film in this study may not well match with the basic assumptions of the JMA model. According to the JMA model, the monoclinic grains should grow linearly with constant growth rate, and the growth is a thermally activated process which can be described by Arrhenius law. Thus, a larger grain size and the higher monoclinic fraction are expected for Hf<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> thin films annealed at higher temperature. However, from the experimental observations in this study, no increase in grain size could be observed with increasing annealing temperature, and the median grain radius is only ~7 nm which should be too small to be considered as grain growth according to the JMA model. Toriumi et al.<sup>[S1]</sup> applied the JMA model to the cubic to monoclinic phase transition in 10 nm-HfO<sub>2</sub> films according to equation S1 for the monoclinic phase fraction r<sub>m</sub>.

$$\Delta r_{\rm m} = 1 - \exp[-(bt)^{\rm n}] \tag{S1}$$

In equation S1, b, t, and n are the growth rate of the grain boundary, time, and dimension of growth, respectively. They could extract an n value of 0.3, which seems unreasonably small compared to what is generally achieved for bulk ceramics. In Chevalier's work on bulk ceramic <sup>[S2]</sup>, the n value is 3.6 which is certainly reasonable for the three-dimensional growth of nuclei. An n value even smaller than 1 is known to be possible when a nucleation process governs the crystallization without grain growth, and a nucleation rate is decelerating during the crystallization process.<sup>[S3]</sup> It is believed that the crystallization process in the present study is quite similar to work by Toriumi et al. However, a rather short time range was examined in which deceleration in nucleation rate might be much weaker in this study. Therefore, a constant nucleation rate was assumed, and the crystallization process could be dominated by a nucleation process. The activation energy was estimated from the slope of ln (ln(1- $\Delta r_m$ )<sup>-1</sup>) – 1/T plot as seen in figure 1c of the main text with assuming that n = 1. The n value of 1 can

be observed when the phase transition is dominated by nucleation process, and the nucleation rate per unit volume is constant.<sup>[S3]</sup> Although the nucleation rate per unit volume is constant, the total phase transition rate decreases with increasing time due to the decrease in the relative fraction of the original crystalline phase. The annealing time used in this study (30 s) is much shorter than those in Ref. S1, and the relative fraction of the transformed phase is rather low. Therefore, the assumption of the constant nucleation rate per unit volume should be reasonable for this initial stage of the phase transition.

#### Grain size analysis

Figure S1 (a)-(d) shows the plan-view scanning electron microscopy (SEM) images of  $Hf_{0.5}Zr_{0.5}O_2$  thin films annealed at 400 – 700 °C. For the case of the 400 °C annealed samples, there were some dark spots which can be a source of error in the grain size analysis using the watershed method of Gwyddion software. The watershed method is based on the local minimum determination, and the virtual height of the images are estimated from the image contrast. Therefore, the SEM image of 400 °C annealed sample was not considered to analyze the grain size distribution. Figure S2 (a)-(c) shows the grain size analysis results for 500, 600, and 700 °C annealed samples, respectively, and they are summarized in Figure S3 (a). In Figure S3 (a), no sign of the grain size increase with increasing annealing temperature could be observed. Thus, the grain size distribution of the three samples was averaged in Figure S3 (b).



**Figure S1.** The plan-view scanning electron microscopy images of 9.2 nm-thick  $Hf_{0.5}Zr_{0.5}O_2$  thin films annealed at (a) 400, (b) 500, (c) 600, an (d) 700 °C.



Figure S2. The analyzed part of SEM images in Figure S1b-d.



Figure S3. (a) The grain size distribution of  $Hf_{0.5}Zr_{0.5}O_2$  thin films annealed at 500 - 700 °C and (b) the averaged results.

## Theoretical activation energy calculation

When the material is super-cooled even below the thermodynamic transition temperature, there is a driving force for the phase transition from the high-temperature phase to low temperature. Generally, the phase transition occurred with nucleation and growth, and there is a critical nuclei radius for the spontaneous nuclei growth and resulting kinetic energy barrier. Since the low-temperature phase nuclei are formed within the high-temperature phase matrix, the new interfaces between the two phases are formed. The interface energy increases the free energy of the total system, while the formation of the low-temperature phase decreases the total free energy. As a result, the total free energy can be formulated as equation S2.<sup>[S4]</sup>

$$G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_{LH}$$
(S2)

Here,  $\gamma$  is the interface energy between the two phases and  $\Delta G_{LH}$  is the free energy difference between the high- and low-temperature phases. At the critical nuclei radius  $r_c$ , the free energy has a local minimum value, so the  $r_c$  value can be calculated by differentiating equation S1 by r. When r is  $r_c$ , the activation energy barrier energy can be calculated using equation S1, and the elastic energy due to the volume between the two phases also contribute to the kinetic energy barrier. Equation S3 and S4 show the formulated  $r_c$  and the resulting activation energy per volume of nuclei with critical radius.

$$r_c = -\frac{2\gamma}{\Delta G_{LH}}$$
(S3)

$$\Delta G^{*} = \frac{\Delta G_{LH}}{2} + \left(\frac{1}{2}Y\left(\varepsilon_{11}^{2} + \varepsilon_{22}^{2} + \varepsilon_{33}^{2}\right) + G\varepsilon_{31}^{2}\right)$$
(84)

The right side of equation S3 has a negative sign, but it has a positive value due to the negative value of  $\Delta G_{LH}$  in the super-cooled state. The interface energies between tetragonal and monoclinic and that between tetragonal and orthorhombic phase were assumed to be 0.5 and 0.05 J/m<sup>2</sup>, respectively, from the previous study.<sup>[S5]</sup> The interface energy between orthorhombic and monoclinic phase was assumed to be identical as that between tetragonal and monoclinic phase (0.5 J/m<sup>2</sup>). In equation S4, Y and G are Young's modulus and shear modulus, respectively.  $\varepsilon_{11}$ ,  $\varepsilon_{22}$ , and  $\varepsilon_{33}$  are the normal strains along a, b, and c crystallographic axis, while  $\varepsilon_{31}$  is the shear strain due to the change of  $\beta$  angle. For the calculation of the elastic energy, the lattice parameters and the bulk modulus in a previous study were taken.<sup>[S6]</sup> From the bulk modulus and Poisson's ratio (~0.3), Young's modulus was calculated based on the isotropic solid assumption. Figures S4 (a)-(c) show the critical

nuclei size, activation energy, and exp(- $\Delta G^*/kT$ ) of 9.2 nm-thick Hf<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> thin film, while Figures S4 (d)-(f) show those for the Hf<sub>0.3</sub>Zr<sub>0.7</sub>O<sub>2</sub> thin film.



**Figure S4.** The (a) critical nuclei size, (b) activation energy, and (c)  $\exp(-\Delta G^*/kT)$  as functions of temperature for 9.2 nm-thick  $Hf_{0.5}Zr_{0.5}O_2$  thin film. The (d) critical nuclei size, (e) activation energy, and (f)  $\exp(-\Delta G^*/kT)$  as functions of temperature for 9.2 nm-thick  $Hf_{0.3}Zr_{0.7}O_2$  thin film.

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