Electronic Supplementary Information for

Surface and grain boundary energy as the key enabler to ferroelectricity in nanoscale hafnia-zirconia: comparison of model and experiment

Min Hyuk Park,[a,b] Young Hwan Lee,[a] Han Joon Kim,[a] Tony Schenk,[b] Woongkyu Lee,[a] Keum Do Kim,[a] Franz P. G. Fengler,[b] Thomas Mikolajick,[b,c] Uwe Schroeder,[b,*] and Cheol Seong Hwang[a,#]

[1]Department of Material Science & Engineering and Inter-university Semiconductor Research Center, Seoul National University, Seoul 151-744, Korea.

[2]NaMLab gGmbH, Noethnitzer Strasse 64, 01187 Dresden, Germany.

[3]Chair of Nanoelectronic Materials, TU Dresden, 01062 Dresden, Germany.

(e-mails: [*]Uwe.Schroeder@namlab.com, [#]cheolsh@snu.ac.kr)

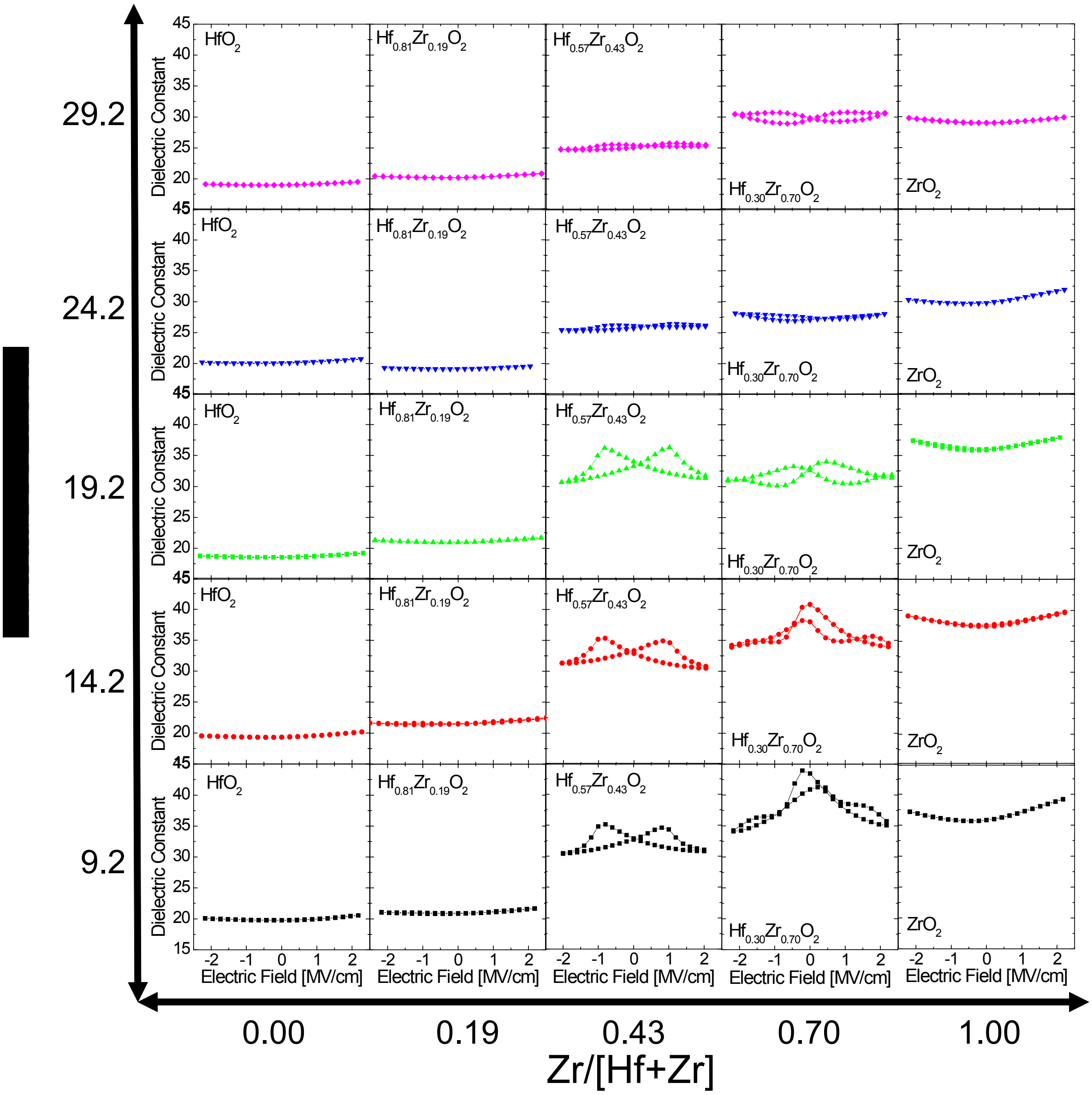

Figure S1. The dielectric constant – electric field curves of HZO films with various composition (Zr/[Zr+Hf]=0.00, 0.19, 0.43, 0.70, 1.00) and thickness (~9.2, 14.2, 19.2, 24.2, and 29.2 nm).

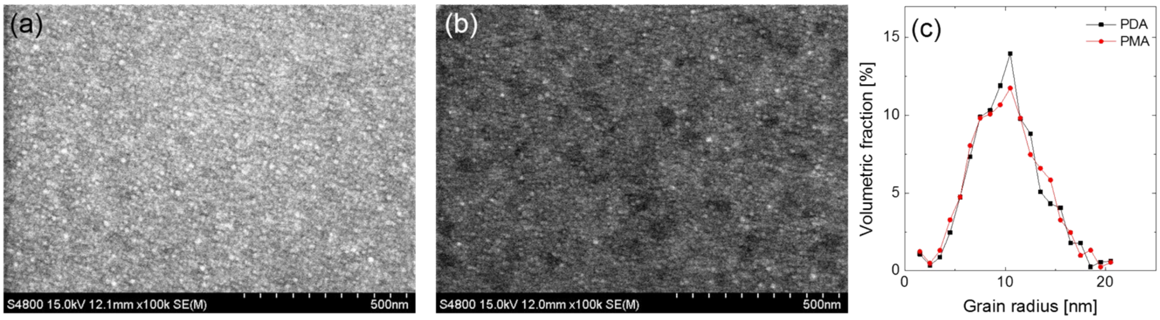

Figure S2. Plan-view scanning electron microscopy images of 9.1 nm-thick $Hf_{0.48}Zr_{0.52}O_2$ film annealed using (a) post-deposition-annealing (PDA) and (b) post-metallization-annealing (PMA). TiN top electrode was removed by wet etching. (c) Grain size distribution of the 9.1 nm-thick PDA and PMA $Hf_{0.48}Zr_{0.52}O_2$ films (extracted from figures S2a and b).

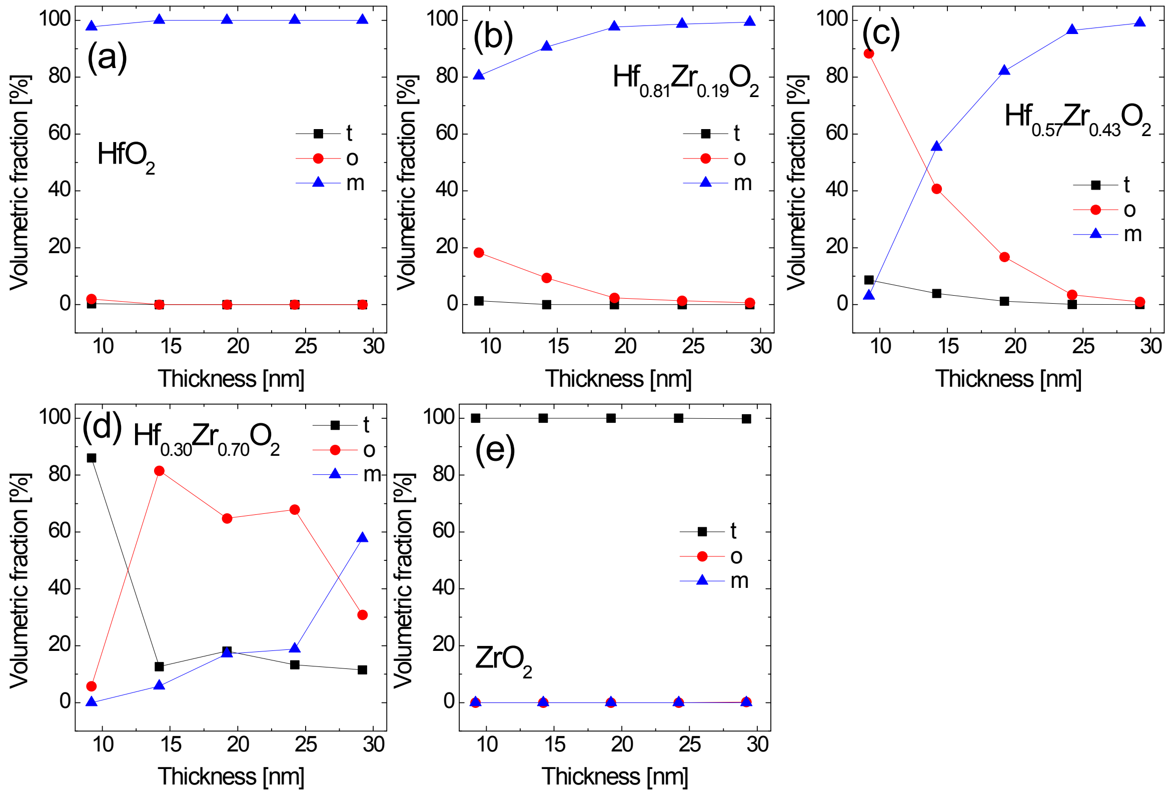

Figure S3. Changes in relative phase fractions estimated based on surface energy model in (a) HfO_2, (b) $Hf_{0.81}Zr_{0.19}O_2$, (c) $Hf_{0.57}Zr_{0.43}O_2$, $Hf_{0.30}Zr_{0.70}O_2$, and (e) ZrO_2 thin films with varying film thickness. (t: tetragonal; o: orthorhombic; m: monoclinic)

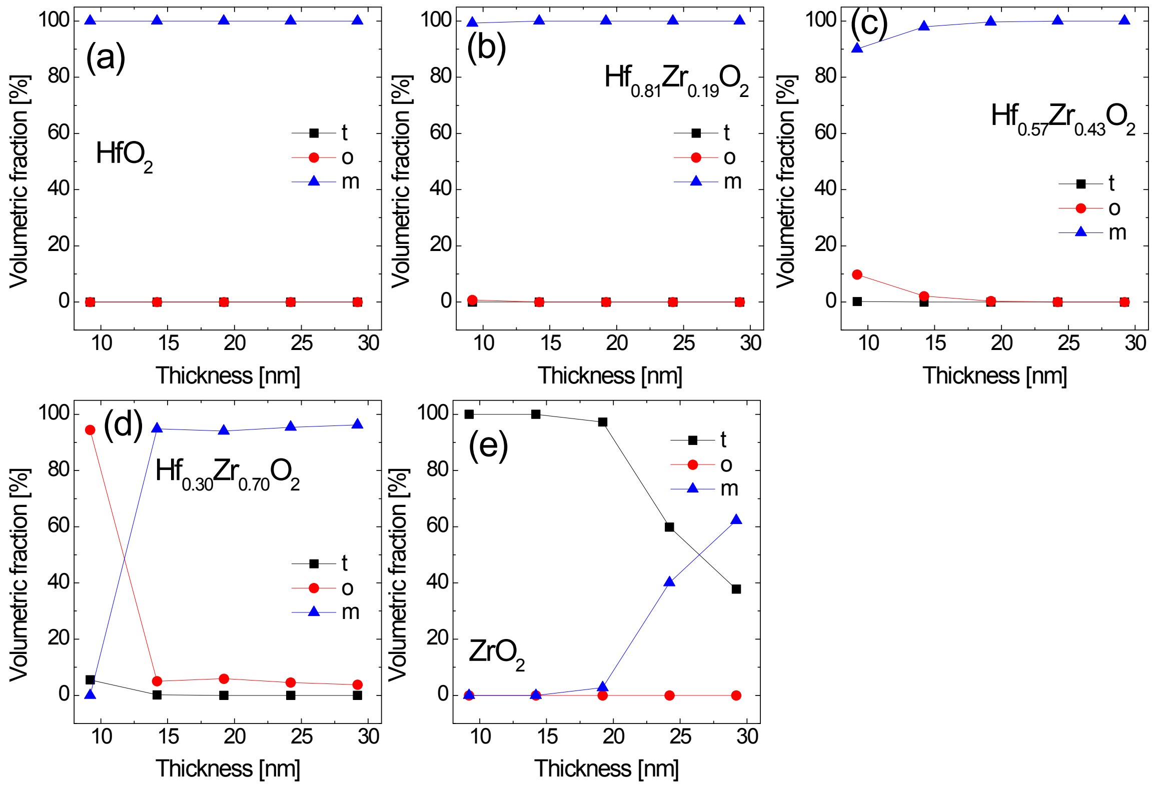

Figure S4. Changes in relative phase fractions estimated based on surface energy model with an assumption of interfacial energy = 0.33 surface energy in (a) HfO_2, (b) $Hf_{0.81}Zr_{0.19}O_2$, (c) $Hf_{0.57}Zr_{0.43}O_2$, $Hf_{0.30}Zr_{0.70}O_2$, and (e) ZrO_2 thin films with varying film thickness. (t: tetragonal; o: orthorhombic; m: monoclinic)

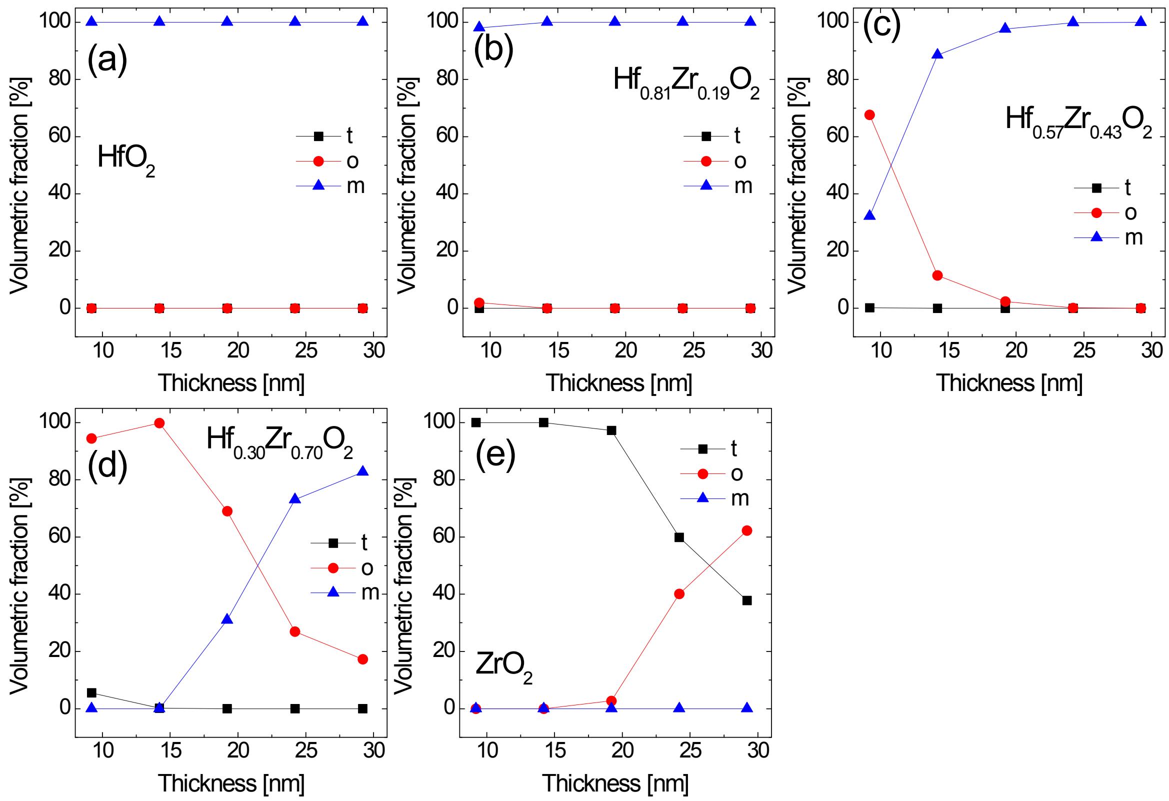

Figure S5. Changes in relative phase fractions estimated based on surface energy model with assumptions of interfacial energy = 0.33 surface energy and TiN capping effect for suppression of phase transition from tetragonal to monoclinic phase in (a) HfO_2, (b) $Hf_{0.81}Zr_{0.19}O_2$, (c) $Hf_{0.57}Zr_{0.43}O_2$, $Hf_{0.30}Zr_{0.70}O_2$, and (e) ZrO_2 thin films with varying film thickness. (t: tetragonal; o: orthorhombic; m: monoclinic)

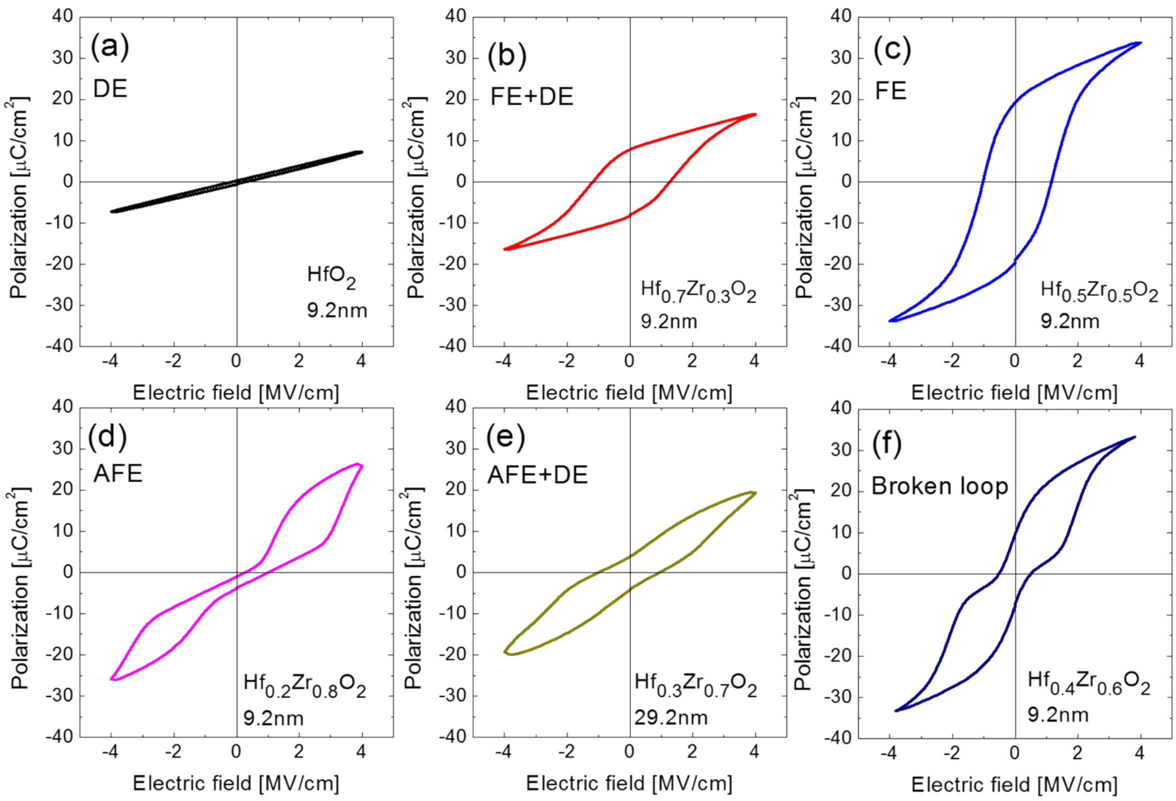

Figure S6. Exemplary polarization-electric field (P-E) curves for electrical performance diagram in figure 7 of the main text. Experimentally measured P-E curves of (a) 9.2 nm-thick HfO_2, (b) 9.2 nm-thick $Hf_{0.70}Zr_{0.30}O_2$, (c) 9.2 nm-thick $Hf_{0.50}Zr_{0.50}O_2$, (d) 9.2 nm-thick $Hf_{0.20}Zr_{0.80}O_2$, (e) 29.2 nm-thick $Hf_{0.30}Zr_{0.70}O_2$, and (f) 9.2 nm-thick $Hf_{0.40}Zr_{0.60}O_2$ films. (DE: dielectric, FE: ferroelectric, AFE: antiferroelectric-like)