

A First-Principles Study on Ferroelectric Phase Formation of Si-Doped HfO₂

IIS, Univ. of Tokyo [○]Jixuan Wu, Fei Mo, Takuya Saraya, Toshiro Hiramoto, and Masaharu Kobayashi

E-mail: jixuanwu@nano.iis.u-tokyo.ac.jp

1. Introduction: Ferroelectric materials have been widely used in low-power memory devices for many years. With the demand for high density, HfO₂-based ferroelectric has been attracting much attention in recent years because it shows ferroelectricity even below 10nm, which is promising for device scaling [1-2]. In this work, to understand ferroelectric phase formation in thermal process, we study fundamental thermodynamics and kinetics of pure and Si-doped HfO₂ at finite size and finite temperature including surface energy, entropy based on first-principles simulation.

2. Simulation method: All simulations are performed with the QuantumATK simulation platform. The exchange-correlation energy is computed with a generalized gradient approximation-Perdew-Burke-Ernzerhof (GGA-PBE). The SG15 Optimized Norm-Conserving Vanderbilt pseudopotential (ONCV) is used for all calculations. The density mesh cut-off is 140 Har. The monoclinic (m, P2₁/c), polar orthorhombic, that is, ferroelectric (f, Pca2₁), non-polar orthorhombic (o, Pbca), and tetragonal (t, P4₂/nmc) phase of HfO₂ are studied.

3. Result and Discussion: Regarding the effect of dopants, we studied how they change the total energy (E_{tot}) as summarized in Fig. 1. Dopants mainly facilitate lowering the energy of the highly symmetric t-phase and have only small effects on the f-phase. We take surface energy and entropy into account to study the finite size and temperature effect. By combining both dopants and surface energy, phase order diagrams are drawn in Fig. 2(b-d). For all cases, the t-phase is the most stable phase for small grain size. As temperature increases, the t-phase becomes stable at larger grain size. Based on the nucleation theory, nucleation starts from the small grain size and is dominated by the lowest-energy phase with reference to amorphous HfO₂ in the beginning of crystallization. [3-4] For pure HfO₂, grain size of the t-phase is very small, which is about twice of a unit-cell lattice even at high temperature. With larger nucleation size, the m-phase can easily prevail in a thin film. With Si dopants, however, the t-phase is stable in large grain size compared to pure HfO₂. In a thin doped-HfO₂ film, the t-phase can nucleate and grows dominantly at high temperature. [5] After t-phase nucleation and growth, when the temperature decreases during cooling-down process, the t-phase is, in turn, not the most stable phase anymore. This indicates that the phase transition may take place from the t-phase to m- or f-phase. Phase transition depends on thermodynamic driving force, which is the free-energy difference between initial and final phases, while kinetics depends on kinetic activation energy as well. Fig. 3 shows the calculated activation energies in which the transition barrier for t→f is much lower than for t→m. This means that phase transition from the t-phase to the f-phase more frequently occurs than m-phase and thus ferroelectric-HfO₂ is formed at low temperature.

4. Conclusion: Based on first-principles calculation, we systematically studied ferroelectric phase formation in pure and Si-doped HfO₂ with the analysis of surface energy, entropy. Dopants play important roles both in the nucleation and phase transition in thermal process.

References

[1] S. S. Cheema et al., Nature, 580(7804), 478-482 (2020), [2] J. Muller et al., Nano letters, 12(8), 4318-4323 (2012), [3] D. A. Porter et al., CRC press (2009), [4] Y. H. Lee et al., Advanced Electronic Materials, 5(2), 1800436 (2019), [5] M. H. Park et al., Advanced Electronic Materials, 4(7), 1800091 (2018).

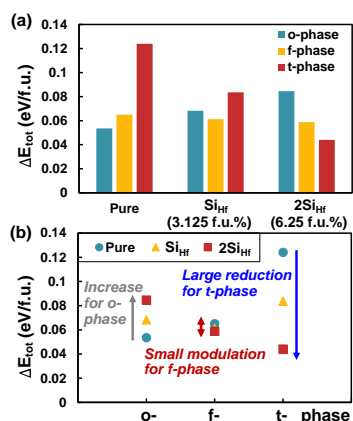


Fig. 1 (a) Total energy calculation in bulk HfO₂ with reference to the m-phase, w/o dopant. (b) Dopants mainly affect the relative energy of the t-phase.

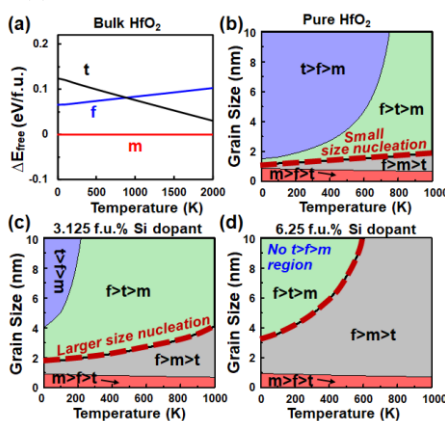


Fig. 2 (a) Free energy of bulk HfO₂ at finite temperature with reference to m-phase. (b-d) Phase order diagrams based on free energy of m, t, and f-phase pure and Si-doped HfO₂ grain.

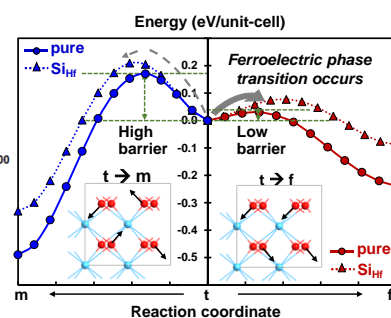


Fig. 3 Energy landscape for phase transition of pure and Si-doped HfO₂ calculated by linear interpolation along the pathway of t→f and t→m. The transition barrier for t→f is much lower than for t→m.