

# DFT MODELS OF NEGATIVE CAPACITANCE

K. Chae<sup>1,2</sup>, K. J. Cho<sup>2</sup>, A. C. Kummel<sup>1</sup>

<sup>1</sup> Dept. of Chem & BioChem, Univ. of Cal., San Diego 9500 Gilman Drive, San Diego CA 92093

<sup>2</sup> Dept. of Mat. Sci., Univ. Texas at Dallas, 800 W Campbell Rd, Richardson, TX 75080-302

E-mail: kichae@UCSD.EDU

## INTRODUCTION

Negative capacitance (or more properly negative differential capacitance) is thought to result from the electrostatic interaction between adjacent layers of a paraelectric and a ferroelectric. The key experimental signature of negative capacitance is a high dielectric constant but an atomic model for this phenomenon in  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  has not been established. Here, DFT calculations are shown which document a paraelectric layer inducing a phase instability in the ferroelectric  $\text{HfO}_2$ , consistent with negative capacitance.

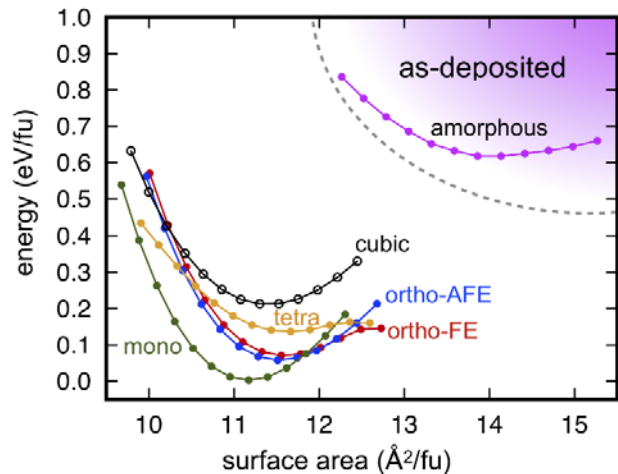
## BACKGROUND

When two dielectrics are in series, the total capacitance can normally be calculated as  $1/C_{\text{tot}} = 1/C_1 + 1/C_2$ . However, as recognized by Khan and Salahuddin, if the ferroelectric and paraelectric are in physical contact, the situation becomes complex because the polarization field from the ferroelectric changes the potential energy of the paraelectric [1]. This electrostatic interaction can be minimized by a change in the ferroelectric layer so it no longer has a dipole pointing perpendicular to the paraelectric layer. If the electrostatic interaction results in the ferroelectric layer having both a similar energy to a second phase and a low barrier to transform to a second phase, this will result in formation of a very high dielectric constant layer consistent with experimental observation of negative differential capacitance which we define as  $C_{\text{tot}} > (1/C_{\text{para}} + 1/C_{\text{ferro}})^{-1}$ . This phase instability of a ferroelectric producing a high dielectric constant has been observed in the well-studied PST system [2]. Here, we show a similar phenomenon in pure  $\text{HfO}_2$  and ordered  $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$  alloy which is a simplified model of HZO.

## DFT OF $\text{HfO}_2$ AND HZO PHASES

DFT was employed to determine the relative stability of the phase of  $\text{HfO}_2$ , HZO, and  $\text{ZrO}_2$  as a function of biaxial tension. For all oxide, the common growth direction of (111) was modeled. For HZO, both random and ordered alloys were modeled and no differences in relative energies were observed, so only the ordered alloy was employed in future calculations. Experimentally, HZO films are deposited by ALD in the amorphous state and usually capped with the top electrode (typically TiN or W), and then annealed into a crystalline state. Therefore, if there is strong bonding at either the top or bottom electrode interfaces, there will be biaxial tension

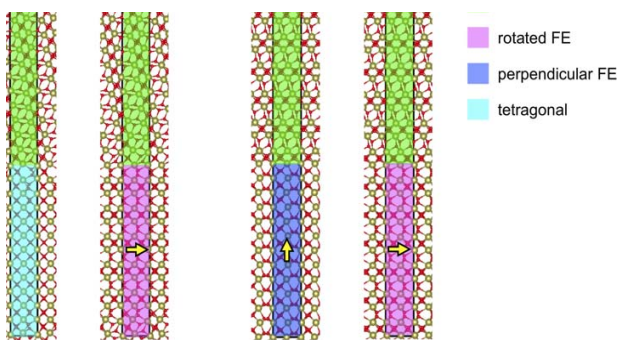
(x-y), but the film will be relaxed in the growth direction (z), i.e., plane-stress condition ( $\sigma_{zz}=0$ ). Consequently, all the calculations were done in plane-stress condition. There are two possible {111} directions for monoclinic; the direction with the highest density of oxygen was chosen since it was hypothesized that it would bond the strongest to the common experimental electrodes such as Si, TiN and W. As shown in Fig. 1, the orthorhombic ferroelectric phase is less stable than the monoclinic phase by 70 meV/fu in the absence of tension. However, only 2.9% biaxial strain is sufficient to make the orthorhombic ferroelectric phase the most stable phase. For  $\text{ZrO}_2$ , similar relative energies and tension effects are observed, but for  $\text{HfO}_2$ , 4.2% tension is needed to stabilize the orthorhombic ferroelectric phase consistent with experimental observation showing it is more difficult to stabilize the ferroelectric phase in  $\text{HfO}_2$  than HZO. For pure  $\text{ZrO}_2$  thin films (5-15nm) or nanocrystalline thick  $\text{ZrO}_2$  films, the antiferroelectric tetragonal phase is often observed [3], but as shown in Fig 1, stress or strain alone cannot stabilize this phase; this is consistent with interfacial free energy or unfavorable electrostatic interactions of the ferroelectric with paraelectric oxide at interfaces, or negative capacitance, stabilizing the non-polar tetragonal phase.



**Fig. 1. DFT Model of Effect of Strain/Tension on the Phase of HZO.** While the ground monoclinic state (green) is the most stable by 70 meV/fu, with 2.9% biaxial tension, the orthorhombic ferroelectric phase (red) become the most stable. Note the commonly observed antiferroelectric tetragonal phase (orange), cannot be stabilized except by unrealistic strain.

## DFT OF STACK STRUCTURES

DFT was employed to model interfaces between the various HfO<sub>2</sub> and HZO phases; below, HfO<sub>2</sub> is shown for simplicity but all trends are similar. On the surface of all common electrodes (Si, W, TiN) an interfacial oxide will be present. This implies that a ferroelectric will be in series with a paraelectric. To model this, the HfO<sub>2</sub> monoclinic paraelectric (001) phase was chosen to minimize the effects of interfacial defect formation so the effects of electrostatic interaction would be unambiguously observed. For the first set of calculations, the unit cell size was fixed in x-y at orthorhombic to mimic the typical experimental conditions under which ferroelectric HZO films are observed. A minimum of 6 unit cells of monoclinic are required to minimize the shear strain for this non-cubic lattice. As shown in Fig. 2, a comparison was made of the interfacial free energy. For this stack of 3 nm, the tetragonal was only 36 meV/fu higher in energy than the orthorhombic ferroelectric phase which is about 40% of the bulk energy difference at cell dimensions in the respective stacks (87 meV/fu). This is due to the lower interfacial free energy of 19.7 vs 31.6 meV/Å<sup>2</sup>. Note that ferroelectric in E2 had the dipole in the most favorable direction; if the dipole were vertical, then the tetragonal would be more favorable as shown in E1.



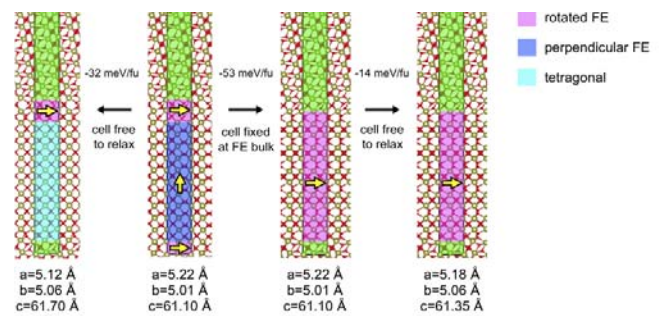
**Fig. 2. DFT 2 Phase Stack Model With Fixed Geometry of HfO<sub>2</sub>.** (a) Using fixed in-plane unit cell size, the interfacial free energy was calculated for monoclinic (001) tetragonal and orthorhombic. E1 has an interfacial free energy of only 19.7 meV/Å<sup>2</sup> while E2 had an interfacial free energy of 31.6 meV/Å<sup>2</sup> thereby reducing the energy difference between the phases to 36 meV/fu. (b) Stack models of monoclinic (010) to orthorhombic ferroelectric phase. When ferroelectric dipole points towards the paraelectric phase, even at 0K, it spontaneously rotates 90 degrees due to a purely electrostatic interaction with the paraelectric phase.

To directly model the effects of the electrostatic interaction, a stack with the dipole in the vertical direction was constructed. In the model of Khan *et al.*, this vertical dipole would raise the overall potential energy of the system. This was observed, and the system spontaneously relaxed by rotating its polarization by 90 degrees at 0K, consistent with a low barrier to phase transformation. If a

field were applied in the vertical direction, the energies E3 and E4 would equalize providing a very high dielectric constant.

## DFT FOR TETRAGONAL STABILIZATION

Because it is energetically unfavorable for the ferroelectric phase to have a dipole perpendicular to any paraelectric interfacial oxide, when the HfO<sub>2</sub> (or HZO or ZrO<sub>2</sub>) film is nanocrystalline, the ferroelectric phase cannot be stabilized, and the tetragonal phase will be the lowest energy cubic phase; this has been observed by Ushakov *et al.* [3]. However, to model tetragonal phase stabilization in thin films, a monoclinic phase was put in series with a ferroelectric phase in which the first monolayer was rotated to stabilize the system (Fig. 3). If the lattice constants along the in-plane directions (x-y) are fixed at that of orthorhombic phase, the remainder of the ferroelectric phase rotates its polarization stabilizing the system by 53 meV/fu consistent with negative capacitance, and the system becomes further stabilized by 14 meV/fu with full cell relaxation. If all lattice coordinates are allowed to relax, the tetragonal phase is spontaneously formed. If a field were applied in the vertical direction, the energies of the tetragonal and ferroelectric configurations would be equalized providing a very high dielectric constant consistent with the basic theory of negative capacitance. If an even greater field is applied, the ferroelectric phase with vertical polarization could stabilize consistent with the common observation that “wake-up” cycles are needed to transform the tetragonal phase into a ferroelectric phase.



**Geometry of HfO<sub>2</sub>.** A stack of monoclinic (001) is in series with ferroelectric with just a monolayer or rotated ferroelectric was modeled with fixed x, y coordinates or with full relaxation. With fixed geometry, the dipole rotates but with full relaxation the remaining ferroelectric phase converts to tetragonal (21 meV/fu).

This work is supported by ASCENT, a SRC program sponsored by JUMP and DARPA.

## REFERENCES

- [1] Asif Khan, PhD Thesis, UC Berkeley
- [2] Park *et al.*, MRS Communications (2018), 8, 795–808
- [3] Ushakov *et al.*, phys. stat. sol. b, 241: 2268 (2004)