Let me explain some basic concepts:

1st is Nudged Elastic band(NEB), NEB is a method for finding saddle points and minimum energy paths between reactants and products, by optimizing a number of intermediate images along the reaction path.

For example, for the HfO2(001), by using NEB method, we can calculate the potential energy changes from HfO2 O to T. First we create a number of intermediate images as shown in this animation, then we use DFT to optimize these intermediates and calculate the energy, we can get this curve here, the potential energy changing along the reaction coordinate. From orthorhombic to tetragonal, the pathway cross the saddle point, with activation barrier about ?eV. the energy different between O and T is ??eV.

2nd the second concept is polarization. In this simple example, one-dimensional chain of charged alternating anions and cations, the lattice constant is a. all ions are in the centers of inversion symmetry, this lattice is non-polar.

But if only look at the ions inside of dashed rectangles, the left edge of the shell as the origin, there is one ion has charge -1 at position a/4, and another ion with charge +1 at position 3a/4, so the polarization, or dipole moment per unit length is

3rd we want to calculated the polarization versus the potential energy changes along the NEB pathways, the system we’re interested are HfO2(001) bulk, 111 bulk, 001 surface and 111 orthogonal from orthorombic P+ through tetragonal to orthorombic P-,

from orthorhombic p+ through Pbcm to orthorhombic P-.

I created all the intermediates as shown in this animation. Thanks JR for providing the structures.

4th I will show the our recent results.

For the pathway from O-Pbcm-O, and O-T-O, Blanka’s recent publication shows that the potential energy versus the polarization along the pathway. The blue curve is O-Pbcm-O, the energy barrier is about 200meV/f.u. the green curve is O-T-O, the energy barrier is 80meV. The Pbcm and tetragonal phase are the non-polar phase, the polarization is zero. The two orthorhombic phase, polarization difference is 25 mc/cm2. This calculation is done by GGA. I am able to repeat this results using GGA functional, as shown in this figure. I also calculate this curve using LDA, the energy barrier is very close the GGA value, but the polarization difference between these two orthorhombic is 10 mc/cm2.

5th this calculation is just for the HfO2 bulk, but in our real system, we use the HfO2(111) slab. Here we use the quantumATK to cleave the (111) HfO2 from 001. The quantumATK provide two options: cleave to the periodic bulk like 111 structure, as shown this figure, the c lattice vector is not perpendicular to the ab plane.

Cleave to the non-periodic slab, the c vector is orthogonal to the ab plane. The following is the QuantumATK code for the cleave function. Thanks KT for asking the vendor for this code.

6th for the bulk 111, we calculate the polarization and potential energy changes along the NEB pathways, the energy barrier and polarization are the same as the bulk 001. Barrier is about ~eV, the polarization of orthorhombic is -50.

7th but for the HfO2(111) slab, the energy difference is about ~eV, which is close to the 001 bulk, but the polarization is very different compared with the bulk 111 or bulk 001.