Supporting Information to

Hafnium-Zirconium Oxide Interface Models with Semiconductor and Metal for Ferroelectric Devices

Kisung Chae[1,2], Andrew C. Kummel[1,*] and Kyeongjae Cho[2,*]
[1] Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA, USA
[2] Department of Materials Science and Engineering, The University of Texas at Dallas, Richardson, TX, USA

Emails: akummel@ucsd.edu, kjcho@utdallas.edu

Effects of Additional Atomic Relaxations at the Interfaces

In this study, the MIM (Fig. 1) and MIS (Fig. 2) stack models are used to investigate the atomic and electronic structures of HZO-metal and HZO-semiconductor interfaces. HZO interface models with Ni and Si are used with the constraint that only bridging O atoms at the interface are relaxed. To verify the accuracy of relaxing just the interfacial O atoms for the models, the effects of relaxing additional interface atomic layers are examined for a subset of validation calculations.

As shown in Fig. S1a, MIM structures show a flat potential profile because the direct contact to the metals compensates excess polarization charges at the interfaces. The charge-compensating effects are unchanged after all the Ni atoms are relaxed, and the potential profile in the FE layer remains flat as seen in Fig. S1b. A slight change in the potential profile at one of the interfaces is observed when all the Ni are relaxed because the potential difference between the HZO and the metal is reduced by atomic rearrangements.

The effects of additional interface atomic relaxations in MIS models are compared in Figs. S1c and S1d. Stack models with DE interlayers are used in this case because subsequent parts of the paper are focused on the effects of thickness scaling studies in the MIS structure with DE interlayers. Additional Si layers at the interface are allowed to relax. The potential profiles for both polarization states are practically identical after the additional relaxation, confirming the validity of the constraint used in this study. Similar to the MIM case, slight change in potential profiles is seen due to the additional relaxations. In sum, the simplified models used in this study capture the overall behaviors in polarization fields without significantly changing the qualitative features in most of the cases and are valid to investigate the isolated effects of electrostatic interactions between the FE and semiconductor.

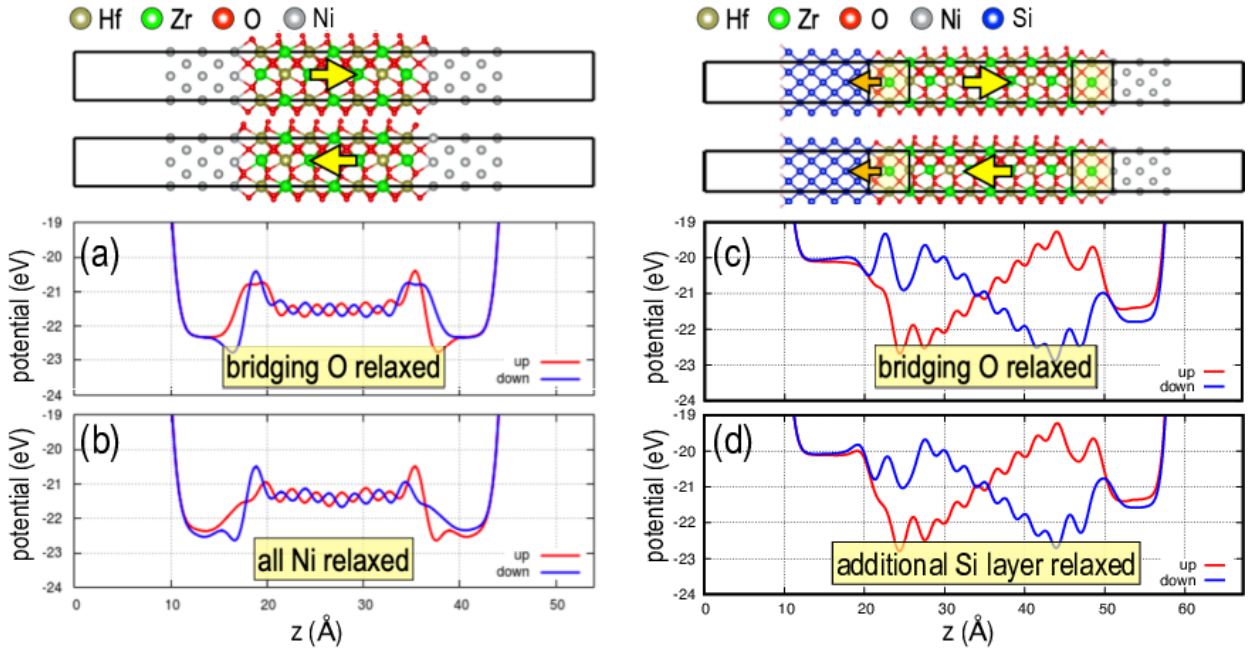

Figure S1. Effects of relaxation range in MIM and MIS structures. MIM with (a) bridging O and (b) bridging O and all Ni relaxed; MIS having DE interlayers with (c) bridging O relaxed and (d) bridging O and an additional Si layer relaxed. With more atoms relaxed, both MIM and MIS still show practically identical potential profiles inside the FE region. This confirms the validity of the constraint used in this study.

Validation and Advantages of a Cubic Phase as a Model DE Layer

In this work, a cubic $Fm\bar{3}m$ phase was used as a model DE layer to mimic the electrostatic interactions between the FE layer and the DE interlayers such as SiO_x and TiON. Because the main purpose of this paper is to investigate the electrostatic role of the DE in the FE device stacks, the cubic phase is expected to play a reasonable role. To validate the hypothesis, potential profiles of the MIS stacks with DE layers of SiO_2 and cubic HZO are compared as in Fig S2. The internal field in the FE is induced due to the SiO_2 DE interlayer at the bottom interface (i.e., Si side) as in Fig. S2(a), which is consistent with the corresponding MIS stack models with cubic HZO DE layer in Fig. S2(b). In addition to the simplicity in developing the atomic models, the additional advantages of the cubic phase are described as follows. First, the cubic phase is the parent fluorite structure of the other phases (e.g., tetragonal, orthorhombic and monoclinic) with highest symmetry, so it is very convenient to generate stack models. However, the ground state monoclinic phase has a non-orthorhombic unit cell, so a large supercell is required to minimize the mechanical strains in the models with periodic boundary conditions, which will significantly increase the computational cost and complexity of the models. Second, the cubic phase induces the least bond strain to the interfaces due to its high symmetry, allowing isolation of the electrostatic effects. With the atomic positions frozen at their equilibrium positions, the cubic phase can serve as the DE layer. This can be considered the best-scenario case of the DE since practical DE layers such as SiO_x at the silicon interface or TiON at the TiN interface. Third, the cubic phase is unambiguously dielectric, while the tetragonal phase, although is non-polar without external bias,

is known as antiferroelectric, which might be confusing. By using the dielectric cubic phase, such confusion can be avoided.

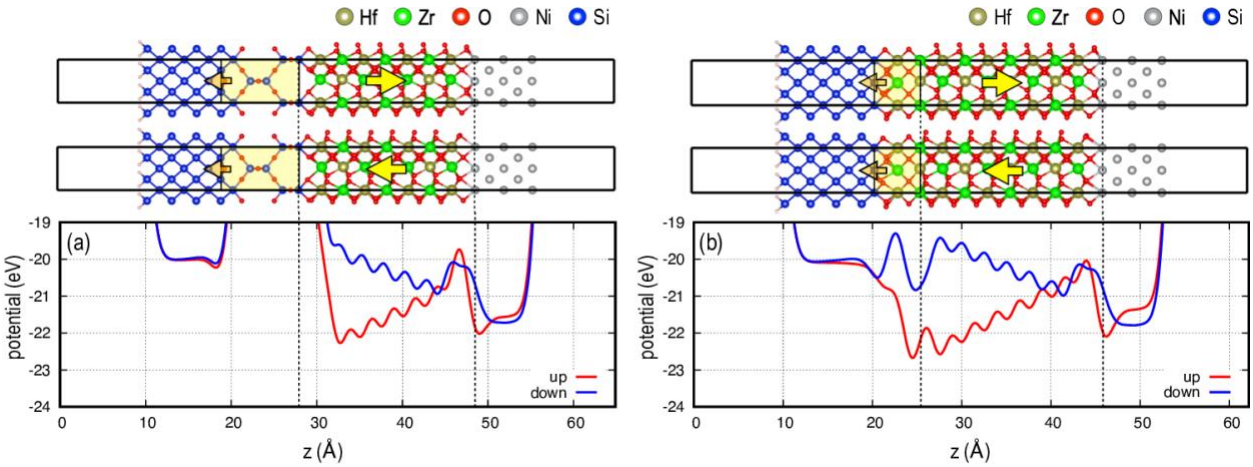

Figure S2. Validation of the cubic HZO phase as a model DE compared to SiO_2. MIS stack models with DE layers of (a) SiO_2 and (b) cubic HZO.

Role of DE interlayers at HZO-Ni and HZO-Si Interfaces

The MIM and MIS stack models with various combinations of DE interlayers are generated to investigate the role of the individual DE interlayers. Figure S2 shows potential profiles for MIM models with various DE interlayer positions. The potential values at either side of the FE layer are predominantly determined by the contact material to which the FE layer is bound and are independent on the type of contact material on the other side of the FE layer. As a result, the internal field strength in the FE region is determined depending on the contact material on either side. As the charge compensating effects of the metal electrodes are deactivated by the DE interlayer, the effects of top and bottom DE interlayers are additive; the internal field strength increases from none to one DE (top/bottom), and further increases with the DE interlayers on both sides. This suggests that fabrication and processing conditions need to be carefully controlled to minimize unwanted DE interlayer formation at the HZO-metal electrode interfaces.

For MIS stacks in Fig. 3, the effect of interlayer DE is more complicated than the MIM stacks in Fig. S2 because there is an interfacial dipole at the Si-HZO interface. The potential values at the bottom side of the FE layer behave quite differently depending on the polarization state in the FE layer. For a polarization up state, both the potential value and field strength are independent of the type of contact material on the bottom side (z~27 Å) whether it is DE or Si, and are solely dependent on the top contact material (z~45 Å) as shown in Fig. 3a. Conversely, the potential profiles are sensitively varied depending on the contact material on both sides as in Fig. 3b similar to the MIM cases. Therefore, a similar additive dipole behavior can be seen for MIS with a polarization down state, while the field strength is solely dependent on presence of the top DE interlayer for a polarization up state. Note that the formation of the DE interlayer at the HZO-semiconductor interface is nearly unavoidable especially for a Si channel, so control of the HZO-metal interface seems critical.

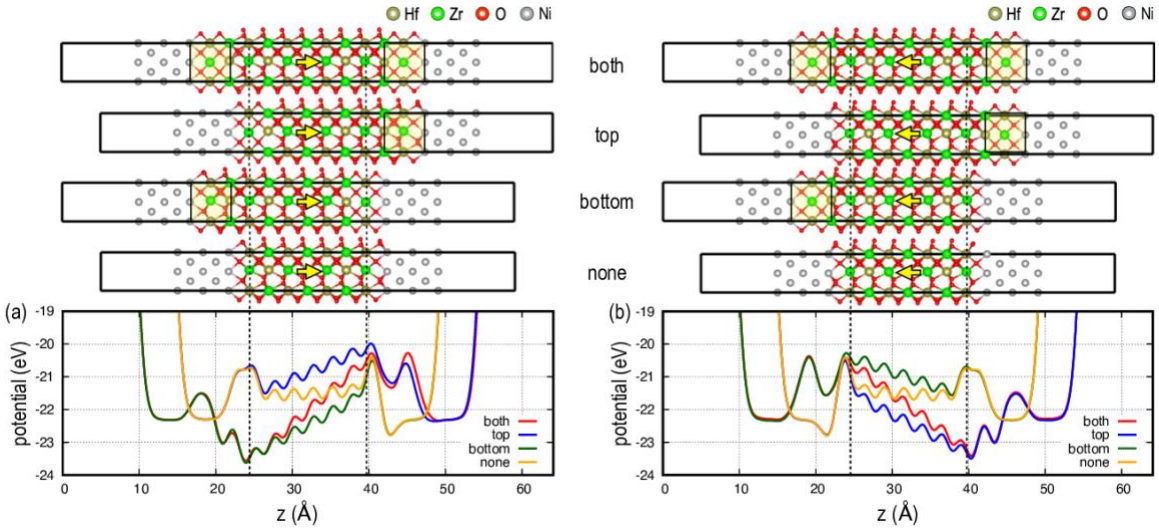

Figure S3. Potential profiles for MIM stacks with various DE interlayer formations: polarization (a) up and (b) down. DE is marked as yellow box, and the FE layer is shown as black dashed lines. Note that the potential values at both top and bottom electrodes remain unchanged regardless of the DE interlayer formation.