P:29 Hole Trapping in Amorphous HfO_2 and Al_2O_3 as a source of positive charging

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Positive charging in $Si/SiO_2/HfO_2$ stacks is usually associated with defects in the interface SiO_2 layer. Implementation of high mobility substrates, such as Ge and III-Vs, will see the gate dielectric exposed to hole trapping. Thin HfO_2 and Al_2O_3 layers deposited on, for example, Ge are usually amorphous [1]. To understand the ultimate behaviour of high-κ dielectrics in such devices we compare hole trapping in crystalline and amorphous HfO_2 and Al2O3 using DFT modelling. Nine periodic models of a-HfO_2, each containing 324 atoms, have been generated using classical MD and a melt and quench procedure. Further optimization of the volume and geometry of these structures was performed using DFT as implemented in the CP2K code [2] with the PBE0-TC-LRC functional. The model a-Al_2O_3 structures produced using the same method and contained 360 atoms.

The trapping of hole polarons on O atoms in m-HfO_2 and α-Al_2O_3 has been previously predicted theoretically [3, 4]. Recent calculations [5] predicted that holes can trap only at three- coordinated O sites in the bulk of m-HfO_2 with a trapping energy of 0.18 eV and with much larger trapping energies at surfaces, featuring two-coordinated O sites. Structural variations, such as under-coordination or elongated bonds, serve as precursor sites where holes can trap spontaneously in a-HfO_2 and a-Al_2O_3 [6]. In both materials over 90% of the hole spin density is localized on two O atoms. The characteristic atomic configurations of the polaron are shown in Fig. 1. The average hole trapping energies (thermal ionization energies) are 1.4 eV in a-HfO_2 and 1.2 eV in a-Al_2O_3. The distribution of hole trapping energies is shown in Fig. 3. We also find that both cells contain up to four precursor sites.

In m-HfO2 two hole polarons form a stable bi-polaron state with the binding energy of 0.65 eV. This state is stabilized by forming of an O-O dimer. In a-HfO_2 the formation of hole bi-polaron takes place spontaneously at structural precursor sites. In both the amorphous and monoclinic cases, the O-O dimer formed has a bond length of 1.5 A˚ . Hole bi-polarons also form in a-Al2O3 again with an O-O bond length of 1.5 A˚ . The relaxation of surrounding ions is asymmetric (Fig. 2). In both oxides this involves ionic displacements exceeding 0.5 A˚ . This large structural reorganisation means that Hf-O, or Al-O, bonds are greatly weakened, suggesting the possibility of further defect creation.

2. Figures

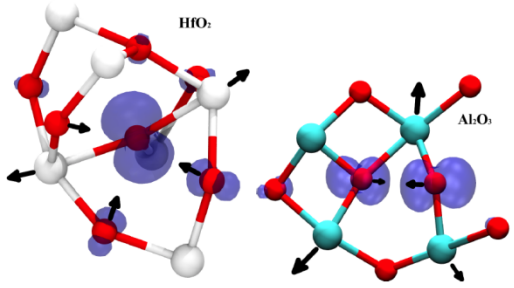

Figure 1. Configurations of hole polarons in a-HfO_2 and a-Al_2O_3. Red indicates O ions, cyan Al ions and white Hf ions. Spin density is indicated by the blue iso-surfaces. Arrows indicate direction of ionic displacements due to polaron trapping.

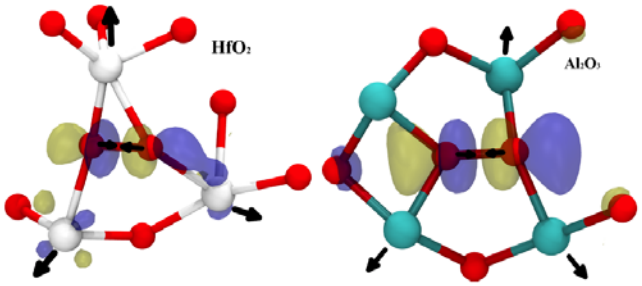

FIGURE 2. Configurations of bi-polarons in a-Al_2O_3 and a-HfO_2. The colored surfaces correspond to the unoccupied KS state of the bipolaron, with blue indicating a positive isovalue and yellow indicating a negative isovalue.

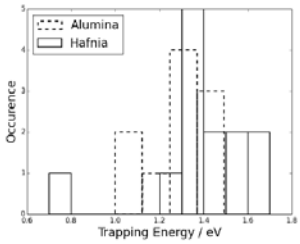

FIGURE 3. Trapping energies of single hole polarons in a-Al_2O_3 and HfO_2. Energies given are referenced to delocalized hole at the top of the valence band.

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