First Principles Computational Studies of High-k Dielectric Stacks for Next Generation Transistors

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The usage of metal-SiO2-Si gate stacks has been pervasive in microelectronic devices for the last four decades. Since continued device miniaturization through physical scaling has reached an impasse, the community is poised for the replacement of SiO2 by HfO2 based "high-K" dielectrics. However, widespread usage of the new high-K gate stack will be hampered due to several troubling issues, attributed to intrinsic O defects in HfO2, as supported by experiments performed at varying levels of O exposure and anneals. In particular, positively charged O vacancies appear to be the most significant and mobile native defects contributing to such unexpected and undesirable behavior.

Concomitant with the above-mentioned technological evolution, the last decade has seen a number of detailed fundamental ab initio computational studies. From a thermodynamic point of view, the most dominant point defects in m-HfO2 are positively charged O and negatively charged Hf vacancies. Kinetic considerations based on the point defect migration barriers in m-HfO2 however indicate that O interstitials are more important than O vacancies as the former have smaller barriers. **Figure 1**, for instance, shows examples of our work aimed at understanding the O vacancy and interstitial defect dynamics close to the Si-HfO2 interface. It can be seen that although both O vacancies and interstitials prefer to segregate to the Si-HfO2 interface (thereby resulting in the formation of interfacial silicides and silicates), O interstitials have much lower migration barriers than O vacancies.

Recently, the more relevant (but also more challenging) amorphous HfO2 (a-HfO2) phase has been investigated using ab initio computational methods. Treatment of the amorphous phase is appropriate not only because the as-deposited phase is amorphous, but also due to the requirement that the HfO2 layer be maintained in the amorphous phase for several reasons. These include better interfaces between a-HfO2 and the Si substrate, isotropy, the lack of grain boundaries of amorphous phases, and compatibility with existing deposition methods.

Here, we present ab initio density functional theory (DFT) based calculations that address the formation and migration of point defects in various charge states in a-HfO2. Since the behaviors of point defects are primarily determined by the local chemistry, which can be quite different in m-HfO2 and a-HfO2, the use of suitable structural models is critical to capture the characteristics of point defects. Our detailed analysis of point defects in various chemical and coordination environments permitted by the a-HfO2 model (**Figure 2**, left panels) lead us to the conclusion that positively charged O vacancies are indeed the most prevalent and mobile point defects (**Figure 2**, right panels)_a conclusion that is expected to persist even when more accurate beyond-DFT computations are utilized.

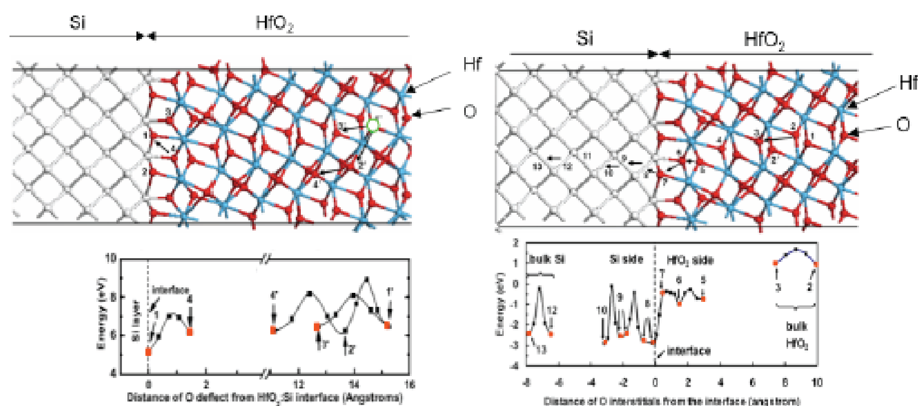

Figure 1: Site-to-site atomic-level migration of O vacancies (left) and O interstitials (right). In both cases, the energy profile in the vicinity of the Si-HfO2 interface is shown in the plots below, and the pathways are shown in the atomic model above.

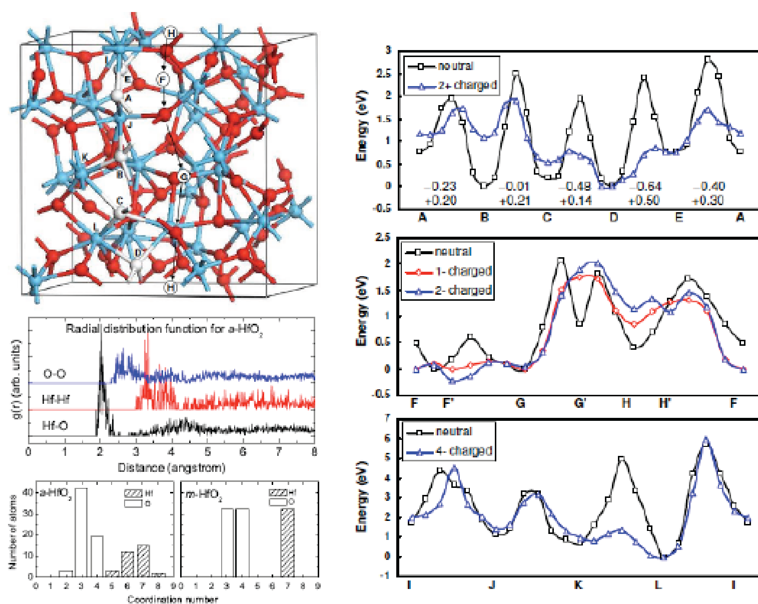

Figure 2: Top, left: Model of a-HfO2, with Hf and O atoms shown in blue and red or white. The long-range migration path for O vacancies is represented by the O sites A-E (highlighted in white), the path for O interstitials schematically by circles F-H, and the path for Hf vacancies by Hf sites I-L. Middle, left: The radial distribution functions for a-HfO2. Bottom, left: Coordination number distribution in a-HfO2 and m-HfO2 containing 32 HfO2 units per supercell. Right: Energy profiles for O vacancy (top), O interstitial (middle) and Hf vacancy (bottom) migration in a-HfO2, along the pathways indicated in the a-HfO2 model (top, left).