Correlated Defect Creation in HfO_2 films

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***Abstract*— Spatially correlated defect generation process has been proposed to be responsible for TDDB Weibull slope measured in HfO_2. We investigated possible mechanisms for correlated defect production in amorphous (a) HfO_2 films under applied stress bias using *ab initio* simulations. During bias application, electron injection into these films leads to the localization of up to two electrons at intrinsic trapping sites present due to the structural disorder in amorphous structures and to formation of O vacancies. Trapping of two extra electrons at a pre-exiting O vacancy facilitate the formation of a new vacancies affecting TDDB statistics and its dependence on the film thickness.**

Keywords*— *DFT calculations; Defect creation, Dielectric breakdown, Amorphous HfO_2

I. INTRODUCTION

HfO_2 films exhibit different degradation kinetics compared to silicon oxides [1]. Understanding the physical mechanisms of BD and their implication on TDDB distributions is crucial for the correct estimation of device reliability and lifetime. Simulations [2] demonstrate that TDDB Weibull slope (β) measured in HfO_2 can be related to the spatially correlated defect generation process. However, the fundamental atomistic mechanisms behind this process are still poorly understood

We used Density Functional Theory (DFT) simulations to propose the mechanism for correlation effects in the time to breakdown statistics of amorphous (a)-HfO_2 films. Calculations for monoclinic HfO_2 [3] demonstrated that formation of neutral oxygen vacancy aggregates is accompanied by small energy gain, which depends on the size and shape of the aggregate. However, the energy barrier for diffusion of neutral O vacancies is about 2.4 eV, suggesting that aggregation of neutral vacancies via diffusion process is too slow to explain degradation and electroforming processes in HfO_2 films.

We demonstrate that two extra electrons trapped at a pre-exiting vacancy facilitate the formation of a new vacancy and an interstitial O^{2-} ion and calculate the energy barriers for defect creation in a-HfO_2. The results suggest that this mechanism can be responsible for correlation effects in the time to breakdown statistics of a-HfO_2 films.

II. METHODS OF CALCULATIONS

Nine periodic models of a-HfO_2, each containing 324 atoms, were generated using classical molecular dynamics and a melt and quench procedure in an NPT ensemble. The volume and geometry of these structures were then fully optimized using DFT as implemented in the CP2K code with the range-separated hybrid PBE0-TC-LRC functional [4]. All calculations were performed in the Γ point using 324 atom periodic cells. The simulation methods and amorphous structures are described in detail in [5]. Briefly, the densities of the DFT optimized a-HfO_2 structures used in this work were in the range of 9.6-9.7 g cm^{-3}. a-HfO_2 samples are characterized by the distribution of Hf and O ion coordination and bond lengths [5]. In particular, around 56% of the Hf atoms are bonded to 6 oxygen atoms, 38% are bonded to 7 oxygen atoms, and 6% to 5 oxygen atoms. On the other hand, 83% of the oxygen atoms are 3 coordinated and 6% of oxygen atoms are 2 coordinated. The band gaps of these initial structures do not contain localized states due to under-coordinated atoms and 6.0 eV on average (ranging from 5.8 to 6.2 eV in different structures).

III. ROLE OF ELECTRON INJECTION

Previous studies have suggested that electron injection into the oxide resulting from bias application can facilitate the formation of Frenkel defects in monoclinic [6] as well as amorphous [7] HfO_2. Structural disorder of a-HfO_2, such as under-coordinated ions and elongated bonds, serve as precursor sites for electron trapping [5]. The electron trapping causes strong Hf–O bond weakening and facilitates thermally activated formation of Frenkel defects: neutral O vacancies and interstitial O^{2-} ions. The barriers for these processes in a-HfO_2 are about 2 eV [6,7]. These barriers depend on local environment and are distributed within 0.5 eV. O^{2-} ions are very mobile with the average barriers for diffusion of 0.5 eV and HfO_2, [6]. The electron trap density of ~$2\cdot10^{21}$ cm^{-3} in a-HfO_2 corresponds to an average distance between precursor sites about 8 Å [7]. However, not all of the traps can trap electrons efficiently. by tunneling from substrate, as some of the traps are higher in energy than others by as much as 0.5 eV. The distribution of trapping energies of single electron traps is approximately 0.5 eV. We show that more O vacancies can be produced as a result of electron trapping at O vacancies.

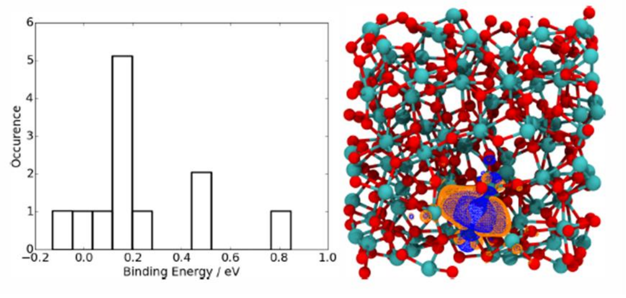

Figure 1. Left: Histogram of the binding energies for di-vacancies in a-HfO_2. A total of 12 configurations were calculated. Positive binding energies indicate 'attraction' between vacancies, whereas negative binding energies indicate repulsion. Right: A typical oxygen di-vacancy configuration for a-HfO_2. Red indicates oxygen and cyan indicates Hf ions. Iso-surfaces of the square moduli of the two (double occupied) di-vacancy states are extended across both of the vacancies, indicating binding between the vacancies.

Our DFT calculations show that, when an O vacancy traps two extra electrons, the formation energy of the second vacancy produced at the nearest neighbor position is lower than that for the first one due to attraction between the vacancies. To study how the interaction between vacancies depends on their mutual position in a-HfO_2, we performed calculations for 12 different configurations. Di-vacancy configurations were produced by first taking a set of four ‘parent’ vacancies. Then, for each parent three di-vacancies were produced by removing adjacent oxygen atoms. The four parent O vacancies were all 3C and were chosen so as to be representative of the average isolated vacancy.

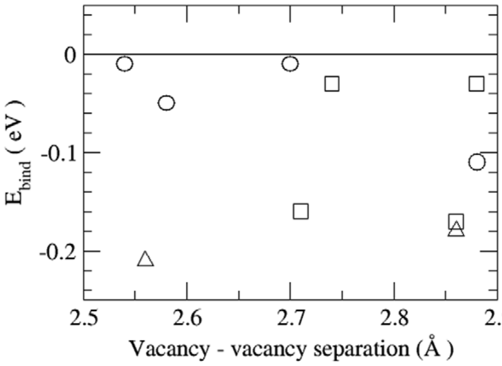

Figure 2. The binding energies of the calculated di-vacancies with respect to the vacancy–vacancy separation [2].

Fig. 1 shows the distribution of binding energies of oxygen vacancies in a-HfO_2. Positive energies indicate vacancy attraction, whereas negative values of a binding energy indicate repulsion. The binding energies are widely distributed with some indicating weak vacancy-vacancy repulsion. However, the average binding energy across the sample is approximately 0.2 eV, suggesting that the formation energy of a neutral vacancy next to a pre-existing one will on average cost 0.2 eV less than the creation of a single, isolated vacancy. The wide distribution of the binding energies, however, indicates that there will be some di-vacancy configurations which are strongly bound and thus very energetically favorable. One configuration, for example, has a binding energy of 0.8 eV. The right panel of Fig. 1 shows two states which are extended across the vacancies in a chemical bond-like fashion. The binding energy distribution for neutral oxygen vacancies as a function of distance is narrow (approximately 0.2 eV, see Fig. 2).

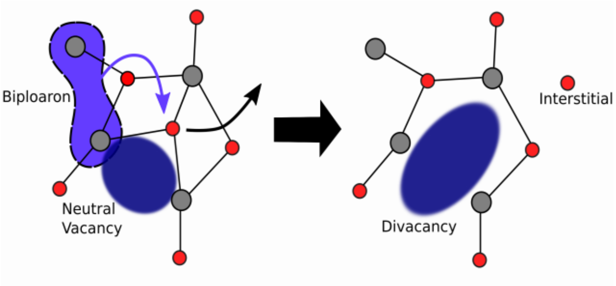

Figure 3. Schematic of the Frenkel pair formation mechanism in a-HfO_2. Red indicates oxygen and grey Hafnium. A bi-polaron trapped on or adjacent to an oxygen vacancy lowers the barrier to form an O vacancy and O^{2-} interstitial pair, similar to the mechanism for the creation of isolated Frenkel pairs [6,7]. The cost to create the di-vacancy, however, is lower.

The correlation effect in O vacancy formation in a-HfO_2 is explained schematically in Figure 3. It shows a doubly negatively charged O vacancy on the left transforming into a di-vacancy and an interstitial O^{2-} ion on the right. The energy cost of creating the second O vacancy is reduced by the presence of a nearby vacancy by about 0.2 eV. Therefore the trapping of electrons onto O vacancies leads to the creation of new vacancies at a lower energetic cost when compared to the creation of original vacancies. DFT calculations with the applied electric field along the O ion displacement path using the modern theory of polarization [8] show that O^{2-} diffusion barriers are significantly reduced in strong fields. These results clearly demonstrate that an applied external field can accelerate the O diffusion to TE.

IV. CONCLUSIONS

We demonstrate that trapping two electrons at O vacancy sites can produce new vacancies at pre-existing vacancies in a-HfO_2. Two extra electrons trapped at a pre-exiting vacancy directly facilitate the formation of a new vacancy and an interstitial O^{2-} ion. These results suggest that, although the mechanisms of O vacancy creation in amorphous SiO_2 and HfO_2 are similar, correlation effects in the time to breakdown statistics of a-SiO_2 and a-HfO_2 films should be different. Using the multi-scale modeling platform presented in [9] allows investigating the impact of the defect correlation on TDDB distribution. One of the most significant results of this study is that increasing the correlation of the defect creation process reduces the dependence of the Weibull slope (β) of TDDB distribution on the layer thickness (t_{ox}). This finding explains the experimental trend observed on β-tox curves observed on SiO_2 and high-k dielectrics [1].

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REFERENCES

[1] Y. Tomura and S. Magita, “TDDB characteristics of thin polycrystalline and smorphous HfO2 films”, 2014 IIRW Final Report

[2] A. Padovani and L. Larcher, “Time-Dependent Dielectric Brekdown Statistics in SiO_2 and HfO_2 Dielectrics: Insights from a Multi-Scale Modeling Approach,” IRPS 2018.

[3] S. R. Bradley, G. Bersuker, and A. L. Shluger, “Modelling of oxygen vacancy aggregatesin monoclinic HfO_2: can they contribute to conductive filament formation?”, *J. Phys.: Condens. Matter*, vol. 27, 2015, pp. 415401.

[4] M. Guidon, J. Hutter, and J. VandeVondele, “Robust Periodic Hartree-Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets” *J. Chem. Theory Comput.* vol. 5, 2009, pp 3010-3018..

[5] M. Kaviani, J. Strand, V. V. Afanas’ev, and A. L. Shluger, “Deep electron and hole polarons and bipolarons in amorphous oxide”, *Phys. Rev*. B, vol. 94, 2016, pp. 020103(R).

[6] S. R. Bradley and A. L. Shluger, “Electron-Injection-Assisted Generation of Oxygen Vacancies in Monoclinic HfO_2”, *Phys. Rev. Appl.*, vol. 4, 2015, pp. 064008.

[7] J. Strand, M. Kaviani, A. L. Shluger, “Defect creation in amorphous HfO_2 facilitated by hole and electron injection.” *Microel. Eng.* vol. 178, 2017, pp. 279-283.

[8] N. A. Spaldin, “Beginner’s Guide to the Modern Theory of Polarization” *J. Sol. State. Chem.*, vol. 195, 2012, pp. 2-22.

[9] A. Padovani, D. Z. Gao, A. L. Shluger, and L. Larcher, “A microscopic mechanism of dielectric breakdown in SiO_2 films: An insight from multi-scale modeling,” *J. Appl. Phys.* Vol. 121, 2017, pp. 155101-10.