A Density-Functional Study of Defect Volatility in Amorphous Silicon Dioxide

Y. Wimmer* W. Goes*, A.-M. El-Sayed*,†, A.L. Shluger†, and T. Grasser*
*Vienna University of Technology, †University College London, UK, Email: wimmer@iue.tuwien.ac.at

***Abstract*—Hole trapping in the gate insulator of pMOS transistors has been linked to a wide range of detrimental phenomena, including random telegraph noise (RTN), 1/ f noise, negative bias temperature instability (NBTI), stress-induced leakage currents (SILC) and hot-carrier degradation. Recently we were able to show that the hydrogen bridge (HB) and hydroxyl E′ centers (H-E′centers) are likely candidates for BTI defects in amorphous silicon dioxide (a-SiO_2). In time-dependent defect spectroscopy (TDDS) measurements, it was observed that defects tend to dis- and reappear in the measurements. This so called *volatility* is not a rare event, but occurs for a majority of the defects. In this work we investigate whether this particular behavior could be explained by an extension of our four-state model. As both of the investigated defect candidates contain hydrogen, we propose that the behavior could be explained by the hydrogen atom moving away from the defect site onto a neighboring oxygen atom and back again. Our results show that the suggested mechanism is likely to occur for hydroxyl E′ centers, but not for the hydrogen bridges.**

I. Introduction

Recently, we have shown that BTI defects can be well described using our four-state non-radiative multiphonon (NMP) model [2, 3]. However, an additional defect feature has been reported [1] which is not covered by this model: defects can become electrically inactive in our measurement window and then become active again randomly over a wide range of time scales (see Fig. 1). This behavior is observed for a majority of the defects and can be triggered by bias switches or by annealing at elevated temperatures. Therefore we suggest extending the four-state model to a six-state model by adding an inactive state 0 in a positively charged (0^+) and neutral (0^n) version (see Fig. 3). Using density functional theory (DFT) calculations in a-SiO_2, we recently have demonstrated that the HB and the H-E′ centers are two likely defect candidates [4–6]. If the hydrogen atom moved away from the defect site this would leave both of the candidates inactive. In the case of the H-E′ center, detachment of the hydrogen leaves a plain silicon-oxygen-silicon bridge, i.e. a defect-free site. For the HB this would create an oxygen vacancy, which can be assumed to be an inactive state, since its defect level lies too low to capture charge under our experimental conditions [4].
Reaction barriers for the hydrogen moving away from the defect site and onto a neighboring oxygen atom (which we refer to as H-relocation) are expected to be close to the energy needed for defect dissolution. For the neutral case, these were calculated in [5]. Since we found significantly lower values for the H-relocation barriers starting from the positive state, in this work we will focus on the positively charged defects. However, also calculations for the neutral transitions will be discussed briefly.
In the following we will investigate the energy barriers of a H-relocation in the positively charged state. This yields a new configuration 0^+ at the neighboring oxygen atom. All calculations were carried out in a-SiO_2, therefore energies and barriers differ from defect to defect resulting in wide distributions. Since time constants for the transitions between different states depend exponentially on the barrier height, we are especially interested if there are barriers lower than $\approx 1\,\mathrm{eV}$ (in absence of stress bias), which would be the barrier that has to be overcome for volatility with a time constant of 1 hour. Applying stress bias significantly changes the barrier height and thereby the time constants (see Fig. 3).

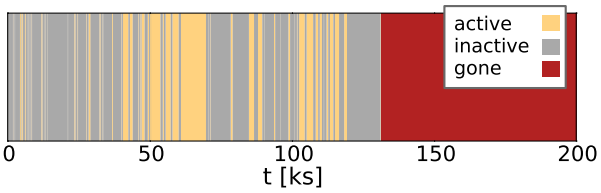

Fig. 1: Measured defect activity of defect I2 extracted from TDDS measurements (as described in [1]) during the first 200 k seconds of the measurement. Defect behavior varies strongly from defect to defect, suggesting a large range of different barrier heights between the active and inactive states.

II. Simulation Framework

For our DFT calculations we used large a-SiO_2 structures consisting of 216 atoms, created using ReaxFF [7]. In this work, three structures containing HBs and four containing H-E′ centers (Fig. 2) were analyzed. All simulations were carried out with the CP2K framework [8], employing the non-local PBE0 TC LRC hybrid functional [9].
For both positive states 2 and 2′ (see Fig. 2), the 15 nearest neighboring oxygen atoms surrounding the defect were determined. The hydrogen atom was relocated from its defect position close to a neighboring oxygen atom (to a distance of $0.8\,\text{Å}$) and the geometry of the system was optimized to create a state 0^+. For the configurations generated based on state 2 it was observed that the hydrogen atom did move back to the defect site in 24% (HB) or 20% (H-E′ centers) of the cases as a result of the optimization of the system. This was not the case for any structure generated from the states 2′ which all remained stable.
All stable configurations 0^+ were then again subjected to geometry optimization in the neutral charged state to create the state 0^n.
Based on the results of those calculations, suitable configurations were chosen for calculating the reaction barriers using the nudged elastic band (NEB) method [10] (see section Results and Discussion).

III. Results and Discussion

As previously mentioned, H-relocation barriers in the neutrally charged state ($1 \rightarrow 0^n$) were found to be considerably higher than in the positively charged counterpart. In the case of the HB, the energy differences ΔE between these two states are already too high. Since the energy barriers for H-relocation are higher or at the very least equal to ΔE, the computationally expensive NEB calculations were not considered necessary. We calculated ΔE for the neutral HB to be $2.56\,\mathrm{eV}$ on average with $\sigma = 0.67\,\mathrm{eV}$, which is comparable to the values published in [5].

978-1-4673-7860-4/15/$31.00 ©2015 IEEE

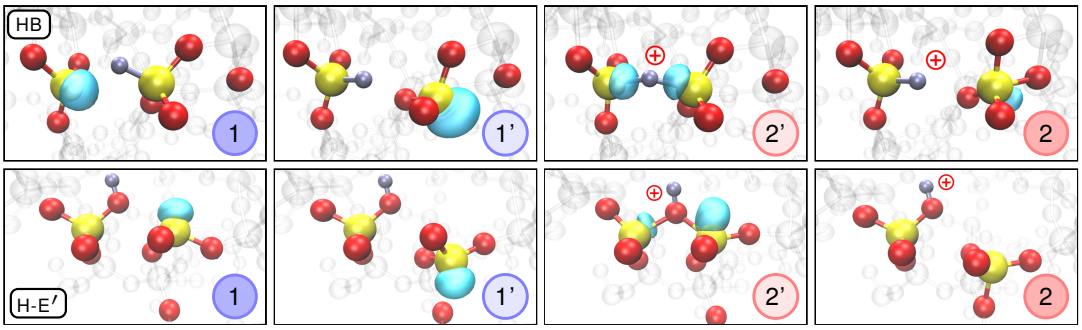

Fig. 2: States 1, 1′, 2′ and 2 for the HB (top) and the H-E′ center (bottom) with H-atoms (silver) Si-atoms (yellow) and O-atoms (red). The localized Kohn-Sham-eigenstate is shown as turquoise 'bubbles'. Upon hole capture the defect can go into the state 2′, the Si atoms move closer together. Depending on the gate bias, the defect either goes back to state 1 or, eventually into the positive state 2 or the neutral state 1′, where the right Si has moved through the plane of its three O neighbors, forming a puckered configuration by bonding to the O in the far right (see Fig. 3).

For the neutral H-E′ center, ΔE between the states is much lower with an average of $0.71\,\mathrm{eV}$ and $\sigma = 0.60\,\mathrm{eV}$. These values appear to be consistent with our experimental observations and thus the corresponding H-relocation barriers were calculated using the NEB-method. The barrier height was on average $1.69\,\mathrm{eV}$ with $\sigma = 0.42\,\mathrm{eV}$. This is again close to the values published in [5]. However, since the barriers in the positive state are significantly lower, in the following we focused on the transitions starting from the positively charged states.

For the positively charged HB there is a huge difference in the energies between the different simulated defects, as can be seen in Fig. 4. As already mentioned above, since these ΔE mark the lower boundary for H-relocation barriers, also here many of those states can be easily ruled out as possible candidates for volatility. Henceforth the computationally expensive NEB calculations were only performed for states with low, or (in the case of the H-E′ center) even negative ΔE.
H-relocation transitions can start from both positive states 2′ and 2. However, NEB calculations clearly showed that for the H-E′ center the defects always undergo the reaction $2' \rightarrow 0^+$, even if E(2′) > E(2). NEB calculations explicitly set up as a transition $2 \rightarrow 0$ all showed similar behavior, namely that the minimum energy path first leads to 2′ before a H-relocation to the state 0^+ occurs. Therefore, for the H-E′ center, only values for the transition $2' \rightarrow 0^+$ are shown in Fig. 4. Furthermore, this figure shows that states 2′ and 0^+ are nearly isoenergetic for the H-E′ centers, with 20% even being slightly lower in energy in state 0^+.
The configurations of state 0 can be divided into three categories, based on their behavior in state 0^n. The relocated hydrogen atom can either remain bonded to the neighboring oxygen, become interstitial, or break up one of the Si-O bonds at its new position, resembling state 1 of the H-E′ center (see Fig. 5). Tab. I shows the probability for these different states 0^n to occur for the different defect candidates.
It should be noted that the energy difference ΔE between states 2′ and 0^+ for defects becoming interstitial in 0^n (Fig. 5 bottom) is on average lower by $0.11\,\mathrm{eV}$, nearly equally high for sticking 0^n (+0.01 eV) (Fig. 5 top) and $0.09\,\mathrm{eV}$ higher for O-Si breaking 0^n (Fig. 5 middle).

Candidate	Sticking	O-Si Breaking	Interstitial
HB	78%	20%	2%
H-E′	36%	28%	36%

Tab. I: Relative occurrence of the different states 0^n (see Fig. 5) for the two defect candidates.

However, the possibility of the transition 2 (2′) $\rightarrow 0^+$ is not determined by ΔE of the initial and final state, but by the barrier E_B between them (see Fig. 3). NEB calculations on selected transitions for the HB showed reaction barriers for $2' \rightarrow 0^+$ ($2 \rightarrow 0^+$) of minimum of $2.54\,\mathrm{eV}$ ($3.03\,\mathrm{eV}$) and an average of $2.83\,\mathrm{eV}$ ($3.65\,\mathrm{eV}$). These values (see Fig. 4 bottom left) are much too high to be able to explain the volatility of the defects. We can therefore conclude that the HB is an unlikely candidate for the proposed volatility mechanism.
Fig. 6 shows the barriers for the reaction $2' \rightarrow 2$ for the H-E′ centers. One can see that the average reaction barrier is lowest for interstitial states 0^n ($1.49\,\mathrm{eV}$) (Fig. 5 bottom), slightly higher for O-Si breaking states 0^n ($1.65\,\mathrm{eV}$) (Fig. 5 middle) and highest for sticking states 0^n ($2.12\,\mathrm{eV}$) (Fig. 5 top). Since the states 0^+ and 2′ appear to be nearly isoenergetic, the behavior for the reverse barriers is similar here. Moreover, there are also barriers with significantly lower energies than $1\,\mathrm{eV}$, that could easily be overcome in experimental conditions, giving a possible explanation for a defect disappearing into inactivity. This makes the H-E′ center a likely candidate for the proposed mechanism.
For the sake of completeness it should be added that for both the HB and the H-E′ center, there is a second possible defect configuration in the four state NMP model, namely if both E(2′) < E(2) and E(1′) < E(1) rather than the other way round as assumed in the default case. This different variant is also found in our DFT calculations and its electrical behavior would be identical and could henceforth not be distinguished in measurements.

Up to now we have only discussed the transitions to the positively charged state 0^+. However, reaction barriers between the states 0^+ and 0^n are also of great interest since the defect would only be electrically inactive if the barrier E_f to get to state 0^n is high enough (see Fig. 3). If this is not the

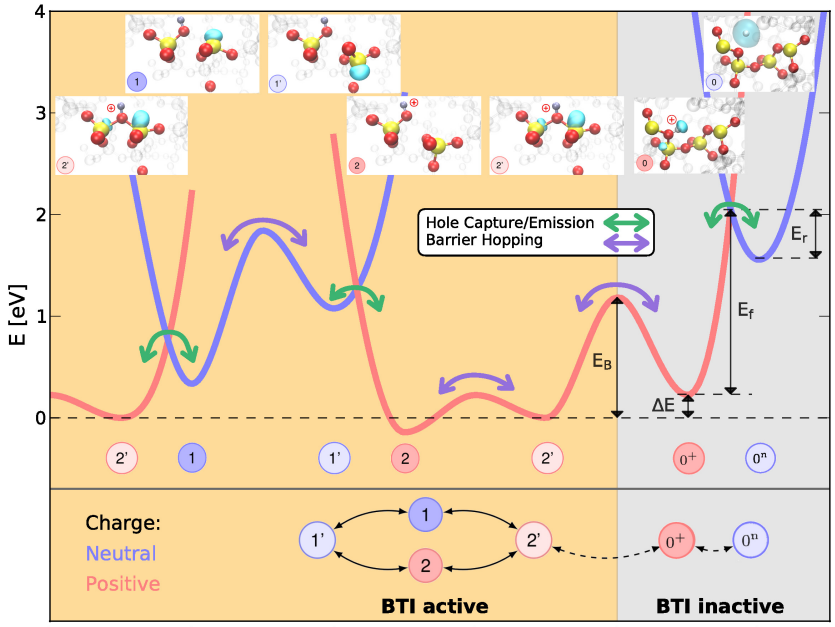

Fig. 3: Example of a cut through the potential energy surface of a H-E′ center defect along the reaction coordinates between different states. Possible transitions can occur by NMP-transitions (green arrows) or barrier hopping (purple arrows). The defect is BTI-active when on the left side of the plot (orange). When it overcomes the barrier $2' \rightarrow 0^+$ it is BTI-inactive (grey area) and therefore not visible in the measurements, given that the barrier between the states 0^+ and 0^n is too high to be overcome under measurement conditions. Depending on the applied gate bias, the parabolas of the neutral states (blue) will be shifted up or down along the energy axis, thereby changing the barriers and time constants for charge-trapping and emission.

case it would again be electrically active, but when switching between 0^+ and 0^n the defect would act like a two-state defect with rather high forward barrier E_f , but small reverse barrier E_r . Of all studied states 0, only one was lower in energy when neutrally charged (in absence of stress bias). However, this new defect does not have a stable position resembling a state 2 or $1'$ (see Fig. 2) and therefore would not be able to act as new NBTI defect. On average the energy difference between states 0^+ and 0^n is 0.85 eV for interstitial states 0^n, 0.96 eV for O-Si breaking states 0^n and again highest for neutrally sticking states 0^n (1.19 eV). Similar to above, these values only represent the lower boundary for the actual reaction barriers between these states. Therefore we also calculated the transitions for these states. Since this reaction involves charge capture or emission, this is done using the NMP theory [3] and a parabolic approximation for the reaction coordinates in both minima (see Fig. 7). One can see that most of the calculated barriers are high enough that they can hardly be overcome under our measurement conditions, leaving the defect electrically inactive in 0^+ as long as it does not overcome the barrier back to state $2'$ again.

Fig. 3 provides an overview of the shape of the potential energy surface for one defect in the extended model. Depending on the applied bias conditions, the neutral potential energy surfaces (blue) shift relative to the positive ones (red) along the energy axis, changing the barriers between them. Note that in this six-state model there are now three possibilities to leave state $2'$ (to 1, 2 or 0^+). However, if the NMP-barrier $0^+ \rightarrow 0^n$ would be overcome, in the depicted case, the hydrogen becomes interstitial in 0^n. If it then diffuses away, this mechanism would provide a possible explanation for a defect disappearing entirely during measurements, like in Fig. 1 at 131 ks.

IV. Conclusions

It has recently been shown that volatility of defects in silicon dioxide is a common phenomenon, which affects a majority of all the measured defects. For the two recently suggested likely candidates for the BTI defect, the hydrogen bridge and the hydroxyl E′ center, we used DFT calculations to investigate a possible mechanism explaining this dis- and reappearing effect. We suggest the transition of a hydrogen atom from the defect site onto a neighboring oxygen to be the underlying mechanism of this volatility. Our calculations show that for the HB defects this reaction is very unlikely, since the reaction barriers are much too high. However, for the second defect candidate, the H-E′ center, we found barriers lower than 1 eV, which could be overcome under our measurement conditions. Furthermore, the barriers for discharging this new configuration again are on average high enough to leave the defect electrically inactive in this new configuration. This makes the H-E′ center a defect candidate which is able to explain the experimentally observed volatility.

Acknowledgment

The authors acknowledge support by the Christian Doppler Laboratory (CDL) for Reliability Issues in Microelectronics and the European Community's FP7 n° 261868 (MORDRED) and n° 619234 (MoRV).

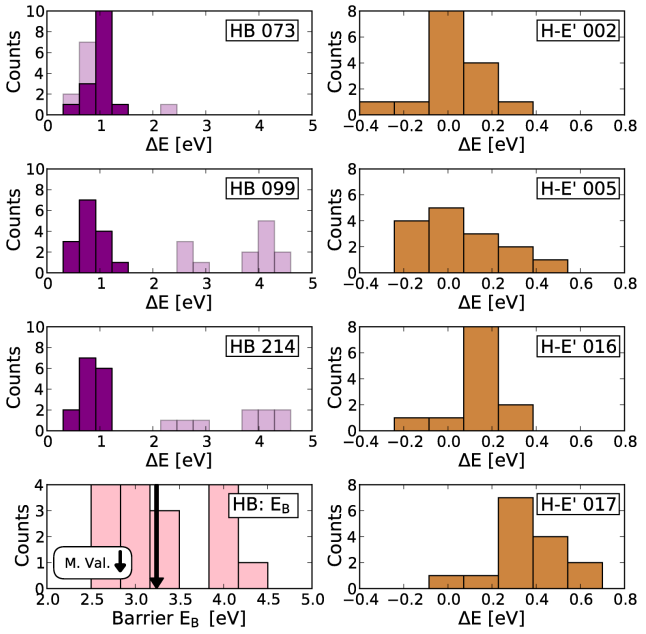

Fig. 4: Energy difference ΔE between the states $0^+ - 2'$ (dark color) and $0^+ - 2$ (light color) for the three investigated structures containing a HB (violet) and the four structures containing a H-E′ center (brown). Since the defect does always prefer the pathway $2' \rightarrow 0^+$ in the H-E′ centers, no $2 \rightarrow 0^+$ data is provided in these graphs. One can clearly see that ΔE is much larger for the HBs. Quite to the contrary 0^+ and $2'$ are nearly isoenergetic for the H-E′ centers, in some cases state 0^+ is even energetically favourable.
Note that not ΔE but E_B defines the probability for H-relocation. E_B for the HB is depicted in the bottom left, being much too high to be overcome during measurement conditions. E_B for the H-E′ center is presented in Fig. 6.

References

[1] T. Grasser, M. Waltl, W. Goes, A.-M. El-Sayed, A. Shluger, and B. Kaczer, "On the Volatility of Oxide Defects: Activation, Deactivation, and Transformation," in *Proc. Intl.Rel.Phys.Symp. (IRPS)*, Jun. 2015.

[2] T. Grasser, H. Reisinger, P.-J. Wagner, W. Goes, F. Schanovsky, and B. Kaczer, "The Time Dependent Defect Spectroscopy (TDDS) for the Characterization of the Bias Temperature Instability," in *Proc. Intl.Rel.Phys.Symp. (IRPS)*, May 2010, pp. 16–25.

[3] W. Goes, F. Schanovsky, and T. Grasser, "Advanced Modeling of Oxide Defects," in *Bias Temperature Instability for Devices and Circuits*, T. Grasser, Ed. Springer, New York, 2014, pp. 409–446.

[4] T. Grasser, W. Gös, Y. Wimmer, F. Schanovsky, G. Rzepa, M. Waltl, K. Rott, H. Reisinger, V. V. Afanas'ev, A. Stesmans, A.-M. El-Sayed, and A. L. Shluger, "On the Microscopic Structure of Hole Traps in pMOSFETs," in *IEDM*, 2014, pp. 530–533.

[5] A.-M. El-Sayed, M. B. Watkins, T. Grasser, V. V. Afanas'ev, and A. L. Shluger, "Hydrogen-Induced Rupture of Strained Si-O Bonds in Amorphous Silicon Dioxide," *Phys. Rev. Lett.*, vol. 114, p. 115503, Mar 2015.

[6] A.-M. El-Sayed, Y. Wimmer, W. Goes, T. Grasser, V. V. Afanas'ev, and A. L. Shluger, "Theoretical Models of Hydrogen-Induced Defects in Amorphous Silicon Dioxide," *Phys. Rev. B*, vol. 92, p. 014107, Jul 2015.

[7] A. van Duin, S. Dasgupta, F. Lorant, and W. Goddard III, "ReaxFF: A Reactive Force Field for Hydrocarbons," *J.Phys.Chem.A*, vol. 105, no. 41, pp. 9396–9409, 2001.

[8] G. Lippert, J. Hutter, and M. Parinello, "A Hybrid Gaussian and Plane Wave Density Functional Scheme," *Molecular Physics*, vol. 92, no. 3, pp. 477–488, 1997.

[9] M. Guidon, J. Hutter, and J. VandeVondele, "Robust Periodic Hartree-Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets," *J.Chem.Theor.Comp.*, vol. 5, no. 11, pp. 3010–3021, 2009.

[10] G. Henkelman, B. Uberuaga, and Jónsson, "A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths," *J.Chem.Phys.*, vol. 113, no. 22, pp. 9901–9904, 2000.

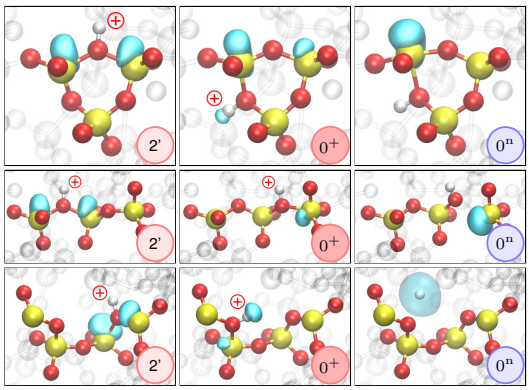

Fig. 5: Examples of different states 0 with different behavior in the neutral state 0^n: Top: The H-atom (white) moves to a neighboring O-atom (red) where it remains attached, also in the state 0^n. Middle: At the O-atom where the H-atom moves to, one of the oxygen-silicon bonds breaks in 0^n. Bottom: The H-atom only sticks to the neighboring O-atom in the state 0^+, but becomes interstitial when charged neutrally (0^n).

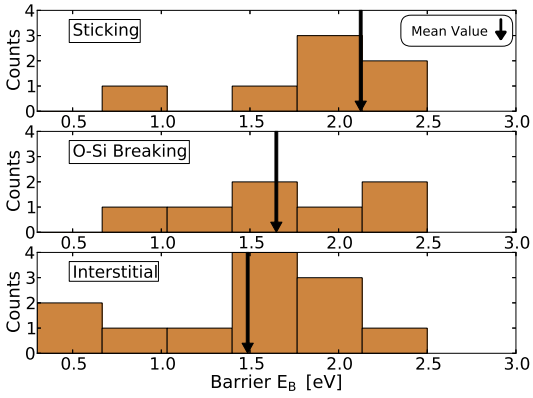

Fig. 6: Barriers E_B for the reaction $2' \rightarrow 0^+$ for the H-E′ centers. Defects are classified by their behavior in the state 0^n, whether they stick at the neighboring atom, become interstitial or break one Si-O bond at the atom they are attached to (see Fig. 5). Even though the mean value for the barrier height (black arrow) still lies above 1.5 eV for all three defect-variants one can also find very low barriers that could easily be overcome during experimental conditions, explaining the defects transition into BTI-inactivity.

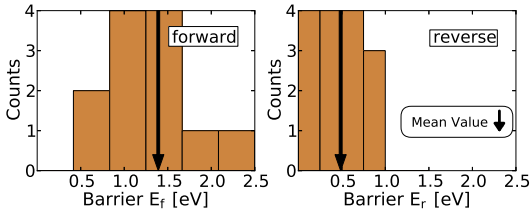

Fig. 7: Barriers E_f and E_r for the reactions $0^+ \leftrightarrow 0^n$ for the H-E′ centers. If the forward barrier (left) is high enough, the defect is electrically inactive. If this is not the case it would be electrically active, but when switching between 0^+ and 0^n behave as two-state defects with much higher forward than reverse barrier. In the simulated defects we find a wide range of forward barriers. Therefore, some defects would become electrically inactive, while others transition between states 0^+ and 0^n.