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On the Evolution of Switching Oxide Traps in the HfO_2/TiN Gate Stack Subjected to Positive- and Negative-Bias Temperature Stressing

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In this paper, evolution of switching oxide traps (SOTs) in the HfO_2/TiN gate stack is examined under positive- and negative-bias temperature (PBT and NBT, respectively) stress. Charging and discharging of SOTs were sensed by repetitive stress/relaxation cycling and the discharging of SOTs was quantified based on the extent of the threshold voltage shift recovery after a fixed relaxation interval. For both the PBT and NBT stress at a low oxide field (~ 5.5 MV/cm), the quantity of SOTs discharged is observed to be approximately constant, independent of the number of stress/relaxation cycles. At a higher oxide stress field (~ 7 MV/cm), however, the quantity of SOTs discharged is seen to decrease progressively with the number of stress/relaxation cycles. This observation implies that a part of the SOTs which can be discharged in earlier relaxation phases is no longer able to do so as the stress progresses. The reduction in recovery points to an increase of the emission times of the trapped charge arising probably from structural changes at the oxide defect sites. Although the evolution of SOTs under both stresses is broadly similar, differences are observed from the opposite gate-polarity relaxation study and stress-induced leakage current measurement. First-principles simulation shows that a defect model based on the oxygen vacancy alone could not explain the differences observed. An extended model involving both the oxygen vacancy and vacancy-interstitial defects is shown to be able to explain the similarities as well as differences observed under PBT and NBT stresses.

Introduction

Bias-temperature instability (BTI) has been a very hot topic since the beginning of the last decade due to its serious impact on the long-term device reliability as the devices are scaled down (1). For the conventional silicon dioxide (SiO_2) or silicon oxynitride (SiON) gate dielectric, nearly all studies were focused on the negative BTI (NBTI) since the impact of the positive BTI (PBTI) was found to be negligible (2). In early work, NBTI was believed to be caused by the generation of interfacial states and the reaction-diffusion (R-D) model was the classical explanation for the phenomenon (3), (4). The predications of the R-D model could match most of the experimental results based on the conventional “stress-measure-stress” (SMS) method. However, later studies showed

that the NBTI effect start to recover significantly once the stress was terminated and the SMS measurement was shown to underestimate the device degradation (5), (6). To minimize the delay between the stress termination and the measurement, numerous “fast” electrical characterization methods have been proposed (7)-(9). With the aid of these fast measurement methods, new observations inconsistent with the R-D model were made. It is now broadly agreed that the NBTI effect is due to the combination of interface state generation and hole trapping at bulk oxide defects (10), (11). Recent studies have also shown that the stress induced interface states are relatively permanent and NBTI recovery within typical experimental time scale is the consequence of the emission of the trapped holes (2), (12).

With the further scaling down of the transistors, the SiO₂ or SiON dielectric has become too thin and the excessive gate leakage current is not acceptable for practical applications (13). To solve the high gate leakage current issue, high-k dielectrics are introduced as a replacement for the conventional SiO₂/SiON dielectric in sub-65 nm technology nodes (14), (15). However, high-k devices also have serious reliability issues, due to the far more defective interface between the high-k dielectric and Si as compared to that between the SiO₂ and Si, as well as the inherently higher density of as-grown oxide defects (16), (17). BTI is certainly one of the most serious and challenging problems since these oxide defects would act as trapping centers for electrons/holes, leading to threshold voltage shift and instability (18). Thus, unlike the SiO₂/SiON gate dielectric, the PBTI effect in the high-k/metal gate transistor is equally or even more serious as compared to the NBTI effect (19). In this paper, we refer to oxide defects that give rise to threshold voltage fluctuations under dynamic gate conditions as switching oxide traps (SOTs) to reflect their transition between the charged and discharged states.

Although the discharging of SOTs is believed to be mainly responsible for the BTI recovery (20)-(21), a systematic study on the topic, especially on the comparison of the response of the SOTs under PBT and NBT stressing, is still lacking. In this paper, we compare the evolution of the SOTs under both NBT and PBT stressing and show the similarities as well as the differences between them. For both the NBT and PBT stressing, the discharge of the SOTs is almost constant, regardless of the number of times the transistor is stressed/relaxed, at a low oxide stress field (~5.5 MV/cm) but it exhibits a progressive decrease at a higher oxide stress field (~7 MV/cm). Results show that the decrease of SOTs density is due to the transformation of SOTs into more permanent oxide defects. However, results from the opposite gate-polarity relaxation study and SILC measurement are found to be different for the NBT and PBT stresses. A possible oxide defect framework is proposed and supported by first-principles simulation.

Experimental and Simulation Details

The test devices (DUTs) were n- and p-MOSFETs fabricated on the same wafer. The gate stacks consist of a 1-nm SiO_x interfacial layer and a 3-nm atomic-layer-deposited HfO₂. The metal gate is TiN. The equivalent oxide thickness (EOT) is approximately 1.4 nm, extracted from capacitance-voltage (C-V) measurement. Fig. 1 shows the C-V characteristics of the n- and p-channel devices. The very similar capacitances in the accumulation regime indicate that the EOTs for both devices are

Figure 1. High frequency capacitance-voltage curves of n-MOS and p-MOS capacitors. The similar capacitances in the accumulation regime imply nearly the same EOT n-MOS and p-MOS devices.

almost the same. The channel length and width for the DUTs are 200 nm and 10 μm , respectively.

The DUTs were subjected to repeated stress and relaxation phases, each lasting 1×10^3 s (i.e. the duty cycle was 50 %). One dynamic BTI (DBTI) cycle consists of one stress phase and the following relaxation phase. The test temperature was fixed at 100 °C. During the stress phase, the applied gate stress voltage was calculated based on the desired average oxide stress field across the gate stack, defined as $(V_g - V_{t0})/\text{EOT}$ (V_{t0} is the threshold voltage of the pre-stress device). During the relaxation phase, the gate voltage was set to either 0 V or at a lower value but of an opposite polarity to that of the stress voltage (1 V for NBTI and -1 V for PBTI). The ultra-fast switching (UFS) method (22), with a very short time delay of 100 ns and almost negligible accumulative recovery effect during the measurement process (23), was employed for transfer curve measurement. Threshold voltage shift (ΔV_t) was extract based on the constant subthreshold current method at a reference current of 15 μA . The fresh V_t was measured before the stress applied. SILC was also measured to monitor oxide (bulk) trap generation.

For the simulation, all calculations were performed by using VASP which employs the plane wave pseudo-potential methods within the density functional theory (24). A hybrid density functional scheme was applied to obtain the correct HfO_2 band gap (25). The ultra-soft pseudo-potentials were used to represent the interactions between the ion core and the valence electrons (26). The exchange correlation functional was treated within the GGA of Perdew, Burke and Ernzerhof (27). In all the calculations, the cut-off energy and k-point were tested to make sure all the calculated results were converged. For the structure optimization, the conjugate gradient method was used and the ion positions were optimized until the residual force was less than 0.01 eV/Å.

The supercell used in our simulation study was amorphous HfO_2 , consisting of 32 Hf atoms and 64 O atoms, with a density of 9.68 g/cm³. The amorphous structure was generated from a cubic HfO_2 structure, via molecular dynamics, following the melt-and-

Figure 2. Evolution of the threshold voltage of an n-MOSFET under certain dynamic PBTI cycles. R denotes the recoverable component of a specific cycle and is defined as the difference of the threshold voltage shift at the end of the stress phase and at the end of the following relaxation phase. P denotes the remnant ΔV_t and is a measure of the part of the SOTs which did not discharge at the end of each relaxation phase. Similar definitions apply for the case of DNBTI.

quench scheme (28). The formation energy E_f of a defect in the HfO_2 was calculated from the total energy E of the defective supercell according to the following formula:

$$E_f(\alpha, q) = E(\alpha, q) - (E_0^0 + n_{\text{Hf}} \mu_{\text{Hf}} + n_{\text{O}} \mu_{\text{O}}) + q(\varepsilon_{\text{F}} + E_{\text{VBM}}) \quad [1]$$

where E_0^0 is system energy of the defect-free supercell and E_{VBM} is the valence band maximum of HfO_2 . For a defect α in charge state q , E_f is a function of the Fermi level ε_{F} and the respective chemical potential of Hf, and O denoted by μ_{Hf} and μ_{O} respectively. The terms n_{Hf} and n_{O} represent the corresponding number of Hf and O atom(s) added/removed from the supercell to form the defect. The charge transition level (CTL) for neutral-to-negative (0/-) and neutral-to-positive (0/+) state transition of the defect were also calculated and are given by the ε_{F} which corresponds to $E_f(\alpha, q) = 0$. The 0/- and 0/+ CTL, measured with respect to E_{VBM} , are akin to trap levels of the defect in the HfO_2 bandgap (25).

Experimental Results and Discussion

Similarities of PBTI and NBTI

Fig. 2 shows the zoom-in view of certain PBTI cycles and the definition of the recoverable (R) component for each DPBTI cycle. R is defined as the difference between ΔV_t at the end of each stress phase and at the end of the following relaxation phase. Since PBTI recovery is due to electron detrapping, the R of each relaxation phase

Figure 3. The evolution of the R (ΔV_t recovery per relaxation phase) during 30 dynamic (a) NBTI (b) PBTI cycles. For both cases, at 5.5 MV/cm, the R keeps almost constant and it decreases progressively when the oxide stress fields increase to 7 MV/cm and above.

is a measure of the discharge of SOTs that were charged up (filled with electrons) in preceding stress phase. Component P denotes the part of ΔV_t remaining and is thus a measure of SOTs which did not successfully discharge at the end of each relaxation phase.

From the evolution of R under the NBT and PBT stress (Fig. 3), the following similarities can be noted for the two cases: (i) at a relatively low oxide stress field (~ 5.5 MV/cm), R is constant, independent of the number of DBTI cycles; (ii) when the oxide stress field is increased to 7 MV/cm and above, R decreases progressively with the number of DBTI cycles. At an even higher oxide stress field (8.5 MV/cm), a greater decrease of R is obtained after a given number of DBTI cycles. Clearly, the apparent change in the R is driven mainly by the increase in oxide field. Charge trapping alone does not cause the decrease of R since this is not observed at the 5.5 MV/cm oxide stress field while electron/hole trapping is still happening.

Since R is a reflection of the part of SOTs which can successfully discharge in a specific DBTI cycle, the constant R at the relatively low oxide stress field may be explained in terms of the detrapping response of a similar group of SOTs that are charged in the preceding stress phase. These SOTs may be considered as “shallow” in terms of energy, i.e. having capture and emission time constants shorter than the period of the stress and relaxation phase. During the stress phase, these traps are “filled” by tunneling electrons/holes. When the stress is removed, the trapped charge can be released or emitted within the duration of the relaxation phase. It should be noted that in past studies involving much thicker oxides, the dispersion in the emission time was explained in terms of the tunneling front model (29). This model stipulates that oxide traps located further away from the Si interface would take a longer time to be discharged, as compared to those nearer the Si interface. In much thinner direct tunneling oxides where the elastic tunneling time is on the order of microseconds, this model fails to account for wide dispersion in the recovery time observed. Thus, it is believed that in these very thin oxides, the discharge time is mainly determined by the

Figure 4. (a) Schematic energy band diagram for the TiN/HfO₂/Si structure showing (i) a detrapping barrier ϕ of a deep electron trap under $V_g = 0$ and (ii) reduction of the barrier by a negative gate bias, which facilitates emission of the trapped electron. (b) Schematic depiction of a deep hole trap, where emission of the trapped hole (via the capture of an electron from the Si substrate) is hindered by the barrier ϕ . Under a positive gate bias, the hole trap is lowered below the Si conduction band and is readily neutralized by an injecting electron. Incremental change (measured w.r.t. the first cycle) of ΔV_t^{eos} (total ΔV_t shift at the end of every stress phase) and ΔV_t^{eor} (the part of ΔV_t shift which did not recover at the end of each relaxation phase) as a function of (a) DNBTI and (b) DPBTI cycles.

Figure 5. Incremental change (measured w.r.t. the first cycle) of ΔV_t^{eos} (total ΔV_t shift at the end of every stress phase) and ΔV_t^{eor} (the part of ΔV_t shift which did not recover at the end of each relaxation phase) as a function of (a) DNBTI and (b) DPBTI cycles.

energy barrier arising out of the difference between the trap state and the Si conduction band edge, as depicted in Fig. 4.

Physically, the progressive decrease of R at higher oxide stress fields implies that a part of the SOTs which could successfully be discharged in the initial relaxation phases is becoming more difficult to be discharged in later relaxation phases. This inference is validated by Fig. 5 (18), (30), in which the incremental change of $|\Delta V_t|^{\text{eos}}$ and $|\Delta V_t|^{\text{eor}}$

(denoted as $|\Delta V_t|^{\text{eos}}$ and $|\Delta V_t|^{\text{eor}}$, respectively) for subsequent DBTI cycles relative to those for the first are examined. It should be noted that $|\Delta V_t|^{\text{eos}}$ is a measure of the total charge trapping at the end of each stress phase. On the other hand, $|\Delta V_t|^{\text{eor}}$ is a measure of the part of SOTs which did not discharge at the end of each relaxation phase, i.e. the P component. At the low oxide stress field (5.5 MV/cm), it can be seen that the rise in $\delta|\Delta V_t|^{\text{eor}}$ is identical to that of $\delta|\Delta V_t|^{\text{eos}}$. This means that the incremental charge trapping per cycle is relatively stable (i.e. it did not discharge within the given relaxation interval) and is responsible for the progressive build-up of the P component¹. On the other hand, $|\Delta V_t|^{\text{eor}}$ is seen to increase much more than $|\Delta V_t|^{\text{eos}}$ under the high oxide stress field. Since the latter is a measure of the total incremental charge trapping, a faster rise in the former indicates that after every cycle, part of the SOTs (which could be discharged during initial relaxation phases) is rendered more permanent (i.e. could no longer be discharged within the given relaxation interval) as the stressing progresses.

We believe that the decrease in R or the gradual transformation of SOTs into a more permanent form entails a shift of the previously shallow trap states to deeper levels (cf. Fig. 4) as the gate dielectric is subjected to a longer period of stressing. The shift of the trap state may be linked to a local structural change that occurs so as to accommodate the addition or loss of an electronic charge at the defect site. The structural change should entail overcoming an associated energy barrier and thus it may not happen so readily under a low oxide stress field. At a higher oxide stress field, field induced lowering of the energy barrier concerned could facilitate the necessary structural change, making it observable within a shorter experimental timeframe.

Differences between PBTI and NBTI

In this section, we discuss two major differences in the evolution of R decrease under PBT and NBT stressing.

BTI studies on SiON and high-k gate MOSFETs have commonly shown that when a stressed device is subjected to a gate relaxation voltage having an opposite polarity to that of the stress voltage, a greater recovery can be achieved as compared to the case when the relaxation is carried out under 0 V. Moreover, it has been shown that a non-negligible abrupt recovery can be further induced by switching the gate to the opposite polarity after the recovery appears to have stopped under the 0 V gate voltage. These results have been explained in terms of electrons/holes captured by deep-level trap states (17), (30)-(33), which require an opposite gate polarity in order for the trapped charges to be emitted (cf. Fig. 4). More importantly, the opposite gate polarity not only induces a faster emission of the trapped charges, it appears to also eliminate the associated defect sites, possibly by a reversal of the local structural change, as the trapping effect is no longer observed in subsequent measurements.

Since the decrease of R has been shown to arise from a part of the SOTs becoming more difficult to be discharged (due presumably to a shift of the trap states to deeper

¹ The origin of this relatively stable incremental charge trapping is not clear. In the case of PBTI, we believe this could be due to the capture of electrons by oxide defects having originally deep energy states (cf. Fig. 4). A similar capture of holes by originally deep hole traps also applies to NBTI but in this case, the contribution of relatively permanent interface state generation would also have to be considered.

Figure 6. The effect of a -1 V gate relaxation voltage on the V_t recovery of an n-MOSFET stressed at (a) 5.5 MV/cm; (b) 7 MV/cm and (c) 8.5 MV/cm. The amount of R decrease (relative to the first DPBTI cycle) is highly suppressed for the latter two cases, in contrast to the case of 0 V relaxation. The R for the 7 MV/cm oxide stress field is in fact constant, as opposed to the decrease observed under the 0 V relaxation.

Figure 7. The effect of a $+1$ V gate voltage on the V_t recovery of a p-MOSFET stressed at (a) 5.5 MV/cm; (b) 7 MV/cm and (c) 8.5 MV/cm. Although the R component is increased as compared to the 0 V recovery, the amount of the R decrease is similar for the two cases, indicating that defect transformation that leads to the decrease in hole detrapping is more permanent than that for PBTI.

levels) as elaborated above, we also examine the impact of an opposite gate relaxation polarity (i.e. instead of a 0 V, a moderate gate voltage of opposite polarity to the stress voltage was applied during the relaxation phase) on the evolution of R decrease. A salient difference between NBT and PBT stresses can be clearly observed. Under the NBT stress, the opposite gate relaxation polarity has almost no influence on the R decrease although the R itself is increased as compared to the 0 V recovery (Fig. 6). However, under the PBT stress, the R decrease at 7 MV/cm oxide stress field, observed under 0 V recovery, is almost completely suppressed by the -1 V recovery (Fig. 7). These results imply that the decrease of R under the NBT stress is largely irreversible whereas it is reversible under the PBT stress. It is speculated that the field induced local structural change associated with electron trapping could be reversed by an opposite oxide field whereas that of the hole trapping case could not.

Another distinct difference is revealed through SILC measurement, carried out after the last DBTI cycle. When R remains constant throughout the DNBTI and DPBTI test,

Figure 8. The impact of 30 DNBTI cycles (at either 0 V or +1 V relaxation) on the p-MOS SILC. No apparent SILC is observed when the R is constant. However, when the R is decreased, a very significant SILC is observed, indicating a significant amount of bulk traps have been generated. This means that the decrease of R is linked to bulk trap generation.

no apparent SILC is measured. However, in the event that the R is decreased, a substantial SILC is measured for the case of DNBTI test (Fig. 8), but not for the case of DPBTI test (Fig. 9). As is the case of the SiON p-MOSFET (34), (35), the R decrease under NBT stress exhibits a strong linear correlation to the SILC generation (i.e. SILC is always observed when R is decreased but is not observed when R is constant). Results also indicate that an opposite gate relaxation polarity has a relatively small impact on the SILC generation observed under NBT stress, meaning that the associated bulk traps are rather stable. This finding is consistent with the results in Fig. 6 which shows that the decrease of R is not affected by the opposite gate relaxation polarity.

On the other hand, only a very marginal SILC is observed for the case of PBT stress at 7 and 8.5 MV/cm (Fig. 9), under which a decrease of R has clearly happened (Figs. 3 and 6). This observation implies that the defect transformation that leads to the increase in the emission times of the trapped electrons did not result in any generation of bulk traps or the bulk traps generated are not active under SILC measurement. This difference from NBT stress, as well as the different impacts of an opposite gate-relaxation polarity on the decrease of R under PBT and NBT stresses (Figs. 6 and 7) suggest: 1) the origins of the oxide defects involved are different in each case or 2) the response of a given oxide defect to hole and electron trapping are different. As will be shown in the next section, a model involving a single defect type could not reconcile the differences between PBT and NBT stress. However, an extended model involving an intermediate state of the defect concerned could reconcile the differences due to the

Figure 9. The impact of 30 DPBTI cycles on SILC on NMOS at 0 V and -1 V recovery. No apparent SILC increase is observed even for the R decrease cases. This indicates the absence of any significant generation of bulk traps in the HfO_2 gate stack over the range of the oxide stress field examined. The results also imply the R decrease involves the conversion of as-grown shallow electron traps into deeper ones by the applied oxide stress field.

different influence of this intermediate defect on carrier transport across the gate stack under positive and negative gate biasing.

Possible Oxide Defect Models

Oxygen Vacancy Defect

Many studies have shown that the oxygen vacancy (V_O) defect is a major source of oxide defects in the HfO_2 (36). Thus, our simulation study will first examine whether the electronic properties of the V_O defect could match, at least broadly, the experimental characteristics of PBTI and NBTI outlined above.

To simulate the formation of the V_O defect, the O atom in-between two Hf atoms is manually removed. The resultant oxygen deficient supercell was then allowed to structurally relax, at 0 K, under the neutral as well as positively and negatively charged states (simulating hole trapping and electron trapping, respectively) until the respective minimum energy state was achieved. The system energy was then extracted for each case. Since the supercell consists of 64 O atoms, a total of 64 V_O defects at different locations in the supercell were created and studied.

Figure 10. (a) Ball and stick diagram of part of the defect-free amorphous HfO₂ supercell used in our simulation study. The supercell consists of 32 Hf atoms and 64 O atoms and was generated by the melt-and-quench scheme; (b) An O atom in-between the two Hf atoms as shown was removed to simulate the oxygen vacancy defect (arrow).

Based on Eq. [1], the CTL for the neutral-to-negative (0/−) and neutral-to-positive (0/+) state transition of each of the 64 V_O defects were calculated and summarized in Fig. 11 (CTL = 0 and 5.4 eV correspond to the E_{VBM} and E_{CBM}, respectively of the HfO₂). Also shown in Fig. 11 are two dashed lines – the top line denotes the E_{CBM} while the bottom line denotes the E_{VBM} of Si. Band offsets between HfO₂ and Si are as indicated. It can be observed that the CTL for the 0/+ state transition of all the V_O defects are situated way above the E_{VBM} of HfO₂ (Fig. 11(a)); the average value is 3.43 eV and the standard deviation is 0.31 eV. This means that V_O's in the HfO₂ could behave as deep-level hole traps under a negative or 0 V gate bias. Moreover, the distribution of the trap states in the upper half of the Si bandgap makes them ideal trap-assisted-tunneling (TAT) centers for electrons tunneling from the metal gate to the Si substrate, as illustrated schematically in Fig. 12(a).

Similar ab-initio simulation of the 0/+ state transition of V_O defects in an amorphous SiO₂ gives an average CTL of ~2 eV (37), i.e. the trap states are situated near the E_{VBM} of SiO₂, way below the E_{VBM} of Si. Thus, unlike the case of the HfO₂, V_O's in the SiO₂ function mostly as shallow hole traps (38), (39). The difference may be caused by the generally greater structural relaxation, following the capture of a hole by the V_O defect in the HfO₂, due to the inherently stronger lattice-electron coupling. Structural relaxation, measured in terms of the mean square displacement of all atoms in the supercell yields 0.4 Å² for the HfO₂, as opposed to the much smaller value of 0.2 Å² for the SiO₂. Thus, we expect that it would be difficult for a reverse transition to the precursor state to take place in the HfO₂ once the structural relaxation associated with hole trapping has occurred. However, a finite energy barrier would have to be first overcome in order for structural relaxation to successfully occur. Barrier lowering by the applied oxide stress field explains the more evident observation of the transformation to permanent hole trapping when the oxide field is increased. Simulation results for the 0/+

state transition could thus explain the decrease in R (Fig. 3(a)) as well as the correlated generation of SILC observed under NBT stress (Fig. 8).

On the other hand, the CTLs for the $0/-$ state transition are situated close to the E_{CBM} of the HfO_2 (Fig. 11(b)). The average CTL is 4.44 eV and the standard deviation is 0.12 eV. This observation indicates the V_O 's in the HfO_2 behaves as very shallow electron traps. Thus, the V_O defect model alone could not satisfactorily explain the increase in permanent electron trapping depicted in Figs. 3(b) and 6, which must necessarily involve much deeper electron traps.

Vacancy-Interstitial Defect

In this section, we show evidence, from ab-initio simulation, that the oxygen vacancy cum oxygen interstitial, i.e. V_O-O_i paired defect in the HfO_2 could function as a

Figure 11. Charge transition level or CTL for the (a) neutral-to-positive ($0/+$) state transition; (b) neutral-to-negative ($0/-$) state transition of all 64 cases of oxygen vacancy defects in the amorphous HfO_2 supercell used in our simulation study.

Figure 12. Schematic energy band diagram of the HfO_2/SiO_x gate stack under (a) negative gate biasing and (b) positive gate biasing. Trap state due to the oxygen vacancy (V_O) and vacancy-interstitial (V_O-O_i) defects are also shown to indicate their roles in trap-assisted tunneling.

Figure 13. (a) Ball and stick diagram illustrating an oxygen vacancy cum oxygen interstitial (V_O - O_i) defect in the amorphous HfO_2 used in our simulation study. The O atom in-between two Hf atoms is manually removed and placed in an interstitial position (O_i) in a nearby region. (b) Schematic energy band diagram of the HfO_2 /Si stack showing the charge transition levels for ten arbitrarily chosen O_i positions. Closely spaced CTLs overlap to give a thick line. Also shown for comparison is the CTL for the V_O defect only.

deep electron trap. Electron spin resonance measurement has detected both oxygen vacancies and oxygen interstitials (O_i 's) in the Hf-based high-k dielectrics (40), (41). Since high-k oxides are generally oxygen deficient, the presence of O_i 's alone is not a likely scenario. However, the generally strong ionic character of high-k oxides implies that field induced displacement of the relatively light O atoms may happen readily in these materials. Thus, the experimental observation of O_i 's suggests that their presence is likely linked to nearby V_O 's. This is the main motivation for our simulation study on the V_O - O_i defect. One could regard the V_O - O_i defect as an intermediate state prior to the formation of the V_O defect, i.e. only when the O_i has moved far away from the V_O site would the V_O defect be formed.

To create the V_O - O_i defect, the O atom in-between two Hf atoms is manually removed and placed randomly in an interstitial position near the V_O defect, as illustrated in Fig. 13(a). Altogether, ten arbitrarily chosen O_i positions were studied for a given V_O defect and the position of the CTL within the HfO_2 bandgap for each of the cases is shown in Fig. 13(b). Interestingly, the CTLs are much lower than those for the V_O defect. Some CTLs are located below the E_{CBM} of Si, indicating that the V_O - O_i defect could function as a deep electron trap. More importantly, the position of O_i , relative to the V_O , is found to have a significant influence on the CTL. For certain positions, the CTLs are relatively shallow (near to the E_{CBM} of Si) while for other positions, the CTLs are deeper. At a certain position studied, the CTL is near the E_{VBM} of HfO_2 , making the defect site a very deep electron trap.

The dependence of CTL on the O_i position is believed to have resulted in a large spread of the CTL across the HfO_2 bandgap and could explain the decrease of R observed under a high oxide stress field (Figs. 3(b) and 6). We reckon that a relatively large oxide field may displace the O atoms relative to the Hf atoms. When the O_i 's are

negatively charged, new metastable states corresponding to deeper CTLs or trap states may be formed, which “lock in” the trapped electrons. An oxide field of the opposite polarity could return the O_i 's to their previous positions. This corresponds to the emission of the trapped electrons and the annihilation of the metastable deep trap states. Similar to the structural relaxation of a single V_O defect, the change in the position of the O atom entails the overcoming of a certain energy barrier. If the barrier is not overcome, the resultant trap states may be less stable (corresponding to shallow CTLs). In this case, the O_i atom would more readily revert to its previous position when the gate stress voltage is removed. This explains the observation of more permanent electron trapping only under a higher oxide stress field.

Treating the V_O - O_i defect as an intermediary prior to the formation of the V_O defect could reconcile the differences observed between PBT and NBT stress. In the former, the moment field induced formation of a V_O - O_i defect occurs, the trap state could be filled by the injecting electrons (Fig. 12(b)). Unless the O_i has moved far enough from the V_O site (which must entail the overcoming of an additional energy barrier), formation of a V_O defect (having a much shallower trap state that functions as a TAT center) could not happen. This may explain why no apparent SILC is observed (Fig. 9) unless at a much higher oxide field that results in the eventual formation of the V_O defect. Meanwhile, it should be noted that the V_O - O_i defect could exist in various intermediate states with the O_i taking different positions around the V_O site. Some of these states are metastable and the correspondingly deep CTLs lock in the trapped electron. For other less stable states (corresponding to shallower CTLs, i.e. nearer the E_{CBM} of HfO_2), the trapped electron would be re-emitted the moment the gate stress voltage is removed. At the same time, the V_O - O_i defect is annihilated with the O_i returning to its previous location. Prolonged stressing increases the probability of transition from a less stable to a metastable state, explaining the increase of the trapped electron emission times or decrease of electron detrapping observed with the number of stress/relaxation cycles (Figs. 3(b) and 6).

On the other hand, the field induced V_O - O_i defects lose electrons to (or capture holes from) the Si substrate under NBT stressing (Fig. 12(a)). As a result of the subsequent structural relaxation that occurs at the defect sites, formation of stable V_O defects may occur if the associated energy barriers are successfully overcome. As the V_O defects have higher CTLs (Fig. 11), they function as efficient TAT centers for electron tunneling from the gate side, thus giving rise to a higher gate leakage (i.e. SILC). It should be noted that metastable V_O - O_i defects with trap states nearer the E_{VBM} of Si also serve as TAT centers for the tunneling holes. The likelihood of V_O defect and metastable V_O - O_i defect formation would likewise increase with the stressing duration or for a given stressing duration, with an increase of the oxide stress field. This explains the corresponding reduction in hole detrapping (Figs. 3(a) and 7), accompanied by SILC generation (Fig. 8), observed. The above explanation offers a plausible physical framework for recent NBTI modeling work involving multiple metastable hole trapping states (42).

Conclusion

The evolution of SOTs in the HfO_2/TiN gate stack subjected to PBT and NBT stressing is examined in detail. Experimentally, it is found that the discharge of SOTs in each relaxation phase remains unchanged at a low oxide stress field, regardless of the number of times the device is stressed and relaxed. At a higher oxide stress field, however, the discharge of SOTs is observed to decrease progressively, indicating that the oxide trapped charge is rendered more permanent as the number of stress/relaxation cycles increases. While these characteristics are similar for both PBT and NBT stress, basic differences are also revealed from opposite gate-polarity relaxation study and SILC measurement: 1) Performing the relaxation under an opposite gate polarity is shown to eliminate or reduce the decrease of SOT discharge for PBT stress but has no apparent effect on the decrease of SOT discharge for NBT stress. 2) SILC generation is always observed when the discharge of SOT is decreased under NBT stress but no SILC generation is observed when a comparable decrease of SOT discharge occurs under PBT stress. First-principles simulation study shows that the V_O defect model is unable to reconcile the differences between PBT and NBT stress. On the other hand, an extended model based on an intermediate $\text{V}_\text{O}\text{-O}_\text{i}$ defect could qualitatively account for nearly all the characteristics of SOT evolution under PBT and NBT stress.

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