Effects of Post-Stress Hydrogen Annealing on MOS Oxides after ^{60}Co Irradiation or Fowler-Nordheim Injection

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Abstract

Changes in interface trap density D_{it} have been determined in MOSFETs as a function of time during hydrogen annealing at 295K. Large increases in D_{it} are observed during H_2 annealing in MOSFETs previously stressed by either ^{60}Co irradiation or Fowler-Nordheim electron injection. The annealing behavior is very similar for both types of stress, which suggests that the D_{it} creation mechanism involves similar chemistry for hydrogen reactions. Studies of the time dependence of D_{it} creation as a function of MOSFET gate length show that the time dependence is limited primarily by lateral diffusion of molecular hydrogen (H_2) through the gate oxide. An activation energy of 0.57 eV, which is consistent with H_2 diffusion, is obtained from the temperature dependence.

INTRODUCTION

When MOS oxides are exposed to various types of stress (irradiation, hot electron or hot hole injection, Fowler-Nordheim injection, etc.), the oxide is damaged by the creation of positive oxide charge Q_{ox} and interface traps D_{it} . It is widely believed that the creation mechanisms are similar or identical for many types of stress, although this has yet to be shown in a rigorous way. Recent research on irradiated oxides has shown that hydrogen is clearly involved in D_{it} creation, and the chemistry of this process is believed to be reasonably well understood [1-5]. However, the mechanism of D_{it} creation by other types of stress is less clear and may be somewhat more complex. For example, studies of D_{it} creation during electron injection suggest that D_{it} creation by recombination of electrons with trapped holes [6,7] is important in addition to hydrogen related mechanisms.

In an effort to elucidate the role that hydrogen may play in D_{it} creation, experiments have been performed wherein MOS oxides are first irradiated and then are exposed to hydrogen (H_2) gas at room temperature [8-14]. In these experiments, large increases in D_{it} are observed during the H_2 exposure; for example, ΔD_{it} during H_2 anneal is typically as large as, or larger than, ΔD_{it} due to irradiation alone. Stahlbush *et al.* [9] have proposed the following mechanism for this effect: (1) Irradiation creates positive charge in the oxide; (2) During the subsequent H_2 anneal, the positive charge reacts with H_2 to create H^+ ions; (3) the H^+ ions drift

to the Si-SiO₂ interface where they react to break Si-H bonds and produce interface traps. In this model, the hydrogen chemistry of trap creation is identical to that which occurs during irradiation itself [1-5]. D_{it} creation during the H_2 anneal occurs over long times from 1 to $>10^6$ s at 295K. Stahlbush and co-workers have proposed that this slow time dependence arises from the slow cracking reaction of H_2 molecules at positively charged defects [10,11]. Alternatively, Mrstik and co-workers have proposed that the rate-limiting step arises from the diffusion of H_2 through the oxide, prior to the H_2 cracking reaction [12,13].

In this work, we have measured D_{it} creation during H_2 annealing. This work has three goals: (1) H_2 annealing measurements have been performed following different types of oxide stress: irradiation, Fowler-Nordheim (FN) electron injection, and channel hot carrier (CHC) degradation. Whether the results obtained for different types of stress are the same or significantly different could help determine if the D_{it} creation mechanisms for the different stress types are the same, or different. Here we will report results for irradiation and FN stress, both of which create *uniform* damage in the oxide. Results for CHC damage, which creates *non-uniform* damage in a region highly localized near the MOSFET drain, are reported elsewhere [15]. We find many similarities in these experiments among the different stresses, but there are also a few instructive differences. (2) This research was undertaken in part to obtain some insight into the chemistry of hydrogen reactions, and to try to resolve the different interpretations of the cause of the time-dependent D_{it} build-up during H_2 anneal (discussed above). Our studies of the time-dependence, gate-length dependence, and temperature dependence show that the time dependence is determined *primarily* (but not exclusively) by the diffusion of H_2 molecules to reaction sites in the gate oxide. Thus, unfortunately, these data do not help much in understanding the hydrogen chemistry involved in D_{it} creation. (On the other hand, these data may yield useful information about the nature of the H_2 diffusion process in gate oxides. Indeed, Mrstik *et al.* [13] have used similar data to show that the H_2 diffusion rate is dependent on MOS oxide thickness and is a factor of 10-100 slower than obtained for bulk silica glass. This result implies that thin gate oxides are slightly densified compared to bulk SiO₂.) We also identify two cases where the time dependence is not due to H_2 diffusion and should be studied further. (3) There are several recent reports of unexpected increases in D_{it} after irradiation [16] or hot carrier stress [17].

Both reports propose that hydrogen-related mechanisms could be responsible for these effects. In this work, hydrogen is deliberately introduced into the oxides to see if effects similar to refs. [16] and [17] are observed.

SAMPLE FABRICATION AND EXPERIMENTAL TECHNIQUES

N-channel MOS transistors were fabricated at NRL with LOCOS field isolation and phosphorus-doped polysilicon gates. Gate oxides were grown in dry O_2 at 900°C to a thickness of 25.4 nm. A few similar results were obtained on N-FETs with a 19 nm dry oxide, and p-FETs with 35 nm dry oxides. All samples were fabricated without inter-metal-level oxides or a final passivation layer; these layers would probably interfere with diffusion of hydrogen into the gate oxide during the hydrogen annealing experiments. Irradiations were performed with a ^{60}Co source with +2.0 MV/cm applied to the MOSFET gates. FN electron injection stresses were performed with about +8 MV/cm applied to the MOSFET gate for 5-10 s to obtain an integrated injected charge of $3.5 \times 10^{16} \text{ e/cm}^2$. Interface trap densities D_{it} were measured using charge pumping (CP) on (typically) $10 \mu\text{m}$ gate length MOSFETs. The CP frequency was $1.5 \times 10^5 \text{ Hz}$ with $1 \mu\text{s}$ rise/fall times and 3-4V ac pulse heights. Using these CP parameters, the D_{it} values given here are midgap values averaged over approximately the central 0.6 eV of the silicon band gap. Initial D_{it} values for unstressed FETs are typically $\sim 1.0 \times 10^{10} \text{ traps/cm}^2\text{-eV}$.

RESULTS AND DISCUSSION

A. Anneal time and gate bias dependence

Charge pumping results for a typical measurement sequence (virgin, post-irradiation, and during H_2 anneal) are shown in Fig. 1. The gate oxide was biased at +2 MV/cm during irradiation and H_2 anneal. The magnitude of the CP current I_{cp} is proportional to D_{it} in the MOSFET, while the voltages at which I_{cp} changes from zero to the maximum and vice versa are related to the MOSFET flatband and threshold voltages. After irradiation, the magnitude of I_{cp} increases, indicating more than an order of magnitude increase in D_{it} , while the negative shift of the curves indicates a buildup of positive oxide charge Q_{ox} . After irradiation, the samples were annealed in 100% H_2 at 295K for up to several weeks. At least 12 hours was allowed to lapse between irradiation and the H_2 anneal to allow any time-dependent changes after irradiation to occur. The increase in D_{it} during the H_2 anneal was measured with CP as a function of anneal time. In general, CP measurements were taken at a single fixed value of V_{base} , where I_{cp} is flat and independent of V_{base} , rather than obtaining the entire I_{cp} curve. This approach is adequate because changes in Q_{ox} are small during the H_2 anneal.

Typical data showing the time dependent increase in I_{cp}

Figure 1. Charge pumping (CP) data showing increase in CP current first after irradiation, and then during subsequent H_2 anneal at 295K. The increase after 24 hours in H_2 is larger than the increase due to the irradiation alone.

during exposure to H_2 at 295K following 1 Mrad(Si) irradiation are shown in Fig. 1. Irradiation causes a large increase in I_{cp} , corresponding to an increase in D_{it} from 0.11 to $1.7 \times 10^{11} \text{ traps/cm}^2\text{-eV}$. A subsequent exposure to H_2 then causes a dramatic further increase in D_{it} . Note that this is not a small effect; ΔD_{it} due to a 24 hr anneal in H_2 is slightly larger than ΔD_{it} due to the irradiation alone. Other annealing experiments in N_2 demonstrate that the time dependent increase in D_{it} is negligible unless H_2 is present. These results make it clear that, at least in our samples, the D_{it} increase in Fig. 1 is not just due to post-irradiation time dependence, as described by Bhat and Vasi [18]. There is a slight movement of the CP curves towards positive V_{base} as the H_2 anneal proceeds, which is due to a small reduction in the radiation-induced positive Q_{ox} .

D_{it} as a function of time during H_2 annealing is shown in Fig. 2. These results were obtained after FN injection, rather than irradiation, but are qualitatively similar for both types of stress (as discussed below). Results are shown for two different MOSFETs from the same chip which were FN-stressed identically ($5 \times 10^{16} \text{ e/cm}^2$ at +19V) but biased differently during the anneal. The initial increase in D_{it} after the FN-stress is about the same in both samples. At long H_2 anneal times, the increase in D_{it} due the anneal is large and about equal to the FN-stress induced increase. In general, ΔD_{it} during H_2 anneal is proportional to ΔD_{it} during the stress; this holds for all types of stress (irradiation, FN-stress, and CHC stress). Results of H_2 annealing after FN stress are generally quite similar to H_2 annealing after irradiation. Different gate oxide fields ($\pm 2 \text{ MV/cm}$) were applied to the two FETs during the H_2 anneal. As shown in Fig. 2, we find that: (1) ΔD_{it} is smaller for negative gate bias, and (2) ΔD_{it} tends to saturate at very long times with negative bias, but not with positive bias. At positive gate bias, D_{it} at very long

Figure 2. Increase in interface trap density D_{it} as a function of H_2 anneal time for two samples stressed by Fowler-Nordheim electron injection of $\sim 5 \times 10^{16} \text{ e/cm}^2$. For positive V_g during anneal (+5.1 V), ΔD_{it} is larger, and a clear saturation is not obtained at long anneal times.

Figure 3. Ratio of post- H_2 anneal increase in D_{it} to the post-stress increase in D_{it} . Samples were either FN-stressed or irradiated under identical conditions, but different gate bias were applied during the H_2 anneal. Irradiation: 1 Mrad(Si) dose with $V_g = +5.1 \text{ V}$; FN injection: $\sim 5 \times 10^{15} \text{ e/cm}^2$. The D_{it} ratio is larger for V_g positive during the H_2 anneal, and appears to be dependent primarily on the direction, but not the magnitude, of V_g .

times increases very slowly, approximately as $\log(\text{time})$. Here we will mostly ignore this effect, whose cause is unknown, and which is a relatively small part of the total D_{it} increase.

The magnitude of ΔD_{it} as a function of gate bias after a long H_2 anneal ($10^5 - 10^6 \text{ s}$) is summarized in Fig. 3 for both irradiation and FN stress. The ordinate in Fig. 3 shows the ratio of ΔD_{it} after H_2 anneal to ΔD_{it} after stress. As noted above, ΔD_{it} due to the H_2 anneal is surprisingly large, and is

about the same as ΔD_{it} created by the stress alone. ΔD_{it} is larger for positive gate bias (the ratio is about 1.3) compared to negative bias (ratio of about 0.75); thus the increase under negative bias is only about 60% that for positive bias. These ratios probably depend on the oxides studied; in previous similar work [9-13], the increase under negative bias is about a factor of 5 smaller than under positive bias. ΔD_{it} is strongly affected by the *direction* of the gate bias, but is relatively independent of its absolute magnitude. There may be a (relatively) small magnitude dependence, but this is hidden in the relatively large scatter in the data. The bias dependencies for FN-stress and irradiation are clearly quite similar. One difference is somewhat greater scatter in the FN stress results (not shown), apparently related to greater variation in the FN injections.

B. Gate length dependence

In an attempt to determine the rate-limiting step of the time dependence shown in Figs. 1 and 2, we have measured the time dependence as a function of the MOSFET gate length L_g . If the rate-limiting step is determined by H_2 diffusion into the gate oxide as proposed by Mrstik [12,13], then the time dependencies should be a strong function of the gate geometry. Experiments were performed on a FET array of devices with the same gate width W_g (29 μm) but different gate lengths L_g ($2 \leq L_g \leq 24 \mu\text{m}$). (Values for L_g were measured on a neighboring chip using a scanning electron microscope with an accuracy of $\pm 0.1 \mu\text{m}$.) The FETs were irradiated to 1.0 Mrad(Si) and then annealed in H_2 at $V_g = -5.1 \text{ V}$. A negative gate bias was chosen to obtain the best saturation characteristic -- see Fig. 2. Fig. 4 shows a plot of the increase in the number of interface traps N_{it} as a function of H_2 anneal time on a log-log scale (note that N_{it} is not scaled to device area).

Results in Fig. 4 show that the increase in N_{it} is independent of gate length at small times (less than about 3000 s), but is strongly dependent on gate length at long times. For short anneal times, ΔN_{it} increases at about the same rate in all FETs. As time increases, saturation is achieved, with the shortest length ($L_g = 2 \mu\text{m}$) FET saturating at the shortest time. Similar (less extensive) behavior was reported by Mrstik *et al.* [13]. This behavior is readily understood if one considers an (abrupt) H_2 diffusion front moving into the gate oxide from the edges of the gate at the MOSFET source and drain (shown schematically in Fig. 5). At first, the amount of diffusion is identical in all devices, independent of gate length, until the two diffusion fronts meet at the center of the gate when saturation is achieved. FETs with longer L_g 's saturate at longer times because of their longer diffusion paths. For this model to be correct, "lateral" H_2 diffusion through the gate oxide must be very much faster than "vertical" diffusion through either the relatively thin poly-crystalline silicon (p-Si) gate on top, or through the underlying crystalline silicon (c-Si) substrate (see Fig. 5). Diffusion of H_2 through the c-Si

Figure 4. Number of traps created during H_2 anneal in FETs with different gate lengths (2-24 μm) and the same gate width (29 μm). Samples were irradiated to 1 Mrad(Si) dose before the H_2 anneal. The N_{it} growth rate is initially the same in all FETs until saturation is achieved in the shortest gate length FET. Each longer FET then saturates at a higher N_{it} level. This behavior is consistent with lateral H_2 diffusion from the edges of the gates towards the center.

Figure 5. Schematic diagram (not to scale) of proposed "lateral" H_2 diffusion through the gate oxide from the edges of the poly gate towards the center.

substrate can clearly be ignored because (a) it is much thicker ($\sim 300 \mu m$) than any gate oxide dimension, and (b) it has a much smaller H_2 diffusion coefficient ($\approx 10^{-15} \text{ cm}^2/\text{s}$ at 295K [19]) compared to the diffusion coefficient in bulk silica glass ($\approx 10^{-11} \text{ cm}^2/\text{s}$) [20]. However, it is not clear that H_2 diffusion through the p-Si gate can be so easily ignored because (a) the p-Si gate is relatively thin ($\approx 0.5 \mu m$), and (b) H_2 diffusion in p-Si may be enhanced by diffusion along the poly-crystalline grain boundaries. However, a recent study of H_2 diffusion in poly thin film transistors (TFTs) [21] concludes that H_2 diffusion is actually retarded at the grain

Figure 6. The D_{it} formation time $\tau_{1/2}$ ($\equiv$ time to create 1/2 the final ΔD_{it}) as a function of gate length. Results are essentially identical for all devices whether irradiated (data from Fig. 4) or FN-stressed. $\tau_{1/2}$ increases rapidly with gate length approximately as $L_g^{1.5}$. Lines show calculated dependencies for 1-dimensional and 2-dimensional models based on H_2 diffusion (see text).

boundaries, and that H_2 diffusion in TFTs occurs primarily by "lateral" diffusion through the gate oxide as shown in Fig. 4.

The dependence on gate length is summarized in Fig. 6, which shows the D_{it} formation time $\tau_{1/2}$ (which is arbitrarily defined as the time required to form 1/2 of the final saturated number of interface traps in each device) as a function of MOSFET gate length L_g . $\tau_{1/2}$ increases strongly with gate length, approximately as $\sim L_g^{1.5}$. This result strongly implies that "lateral" H_2 diffusion through the gate oxide dominates the time dependence, since the time dependence of subsequent hydrogen reactions depends only on the bulk properties of the gate oxide layer, which are independent of gate length. In Fig. 6, results are identical within experimental error for both irradiated FETs (data from Fig. 4) and FN-injected FETs. This suggests that the same mechanism limits the D_{it} formation rate during H_2 annealing for both types of stress -- as would be expected for H_2 diffusion. Finally, essentially the same gate length dependent behavior during the H_2 anneal was observed for positive gate bias, except that $\tau_{1/2}$ is (a) somewhat larger (roughly a factor of 2), and (b) considerably more difficult to determine accurately.

A simple model for the time dependence can be developed assuming a one-dimensional H_2 diffusion model. We assume the H_2 diffusion can be characterized by a sharply defined diffusion front [13,22]. Throughout the diffused region, the H_2 concentration is sufficiently high that the H reactions proceed immediately to completion. In simple diffusion processes, the motion of the diffusion front is

Figure 7. Schematic diagram of 1-dimensional ("1-D") and 2-dimensional ("2-D") H_2 diffusion models. The 2-D model accounts for H_2 diffusion along all four sides of the MOSFET.

proportional to $\sqrt{\text{time}}$, which implies $\tau_{1/2} \propto L_g^2$. Mrstik *et al.* [13] have reported just such a $\sqrt{\text{time}}$ dependence. We also find straight lines if the data are plotted with a $\sqrt{\text{time}}$ abscissa and ΔD_{it} on a linear scale (not shown). However, Fig. 4 does not show $\sqrt{\text{time}}$ dependence because this log-log plot accentuates the region where ΔD_{it} is very small and the diffusion front is probably not sufficiently abrupt compared to the short diffusion distance. In Fig. 6, the predicted L_g^2 dependence (solid line) is compared with experimental data. L_g^2 increases much more rapidly than is observed. This discrepancy is somewhat resolved by using a 2-dimensional model which accounts for diffusion from all 4 sides of the poly gate, which must be considered when the gate length is approximately the same size as the gate width (see Fig. 7). A 2-dimensional model is derived in Appendix A, which gives the *relative* change in $\tau_{1/2}$ based solely on FET geometry (i.e., L_g and W_g). This model is fit to the data at $L_g \ll W_g$ where the 2-D model reduces to a dependence on L_g^2 as expected. For $L_g \approx W_g = 29 \mu\text{m}$, the 2-D model shows that $\tau_{1/2}$ is smaller than expected from the 1-D model because additional diffusion in the 2-D model causes saturation to be achieved more rapidly. Agreement between the 2-D model and the data in Fig. 6 is much improved. However, agreement is still less than satisfactory, especially at $L_g \leq 6 \mu\text{m}$ where the slope should approach L_g^2 in both models, but does not. The reason for the remaining discrepancy is unclear. One source of error is that the FET source and drain are overlapped by $\sim 0.2 \mu\text{m}$ at the edges of the poly gate. Because of the heavy source/drain doping, ΔD_{it} cannot be measured in the overlap region which introduces an error into the value for $\tau_{1/2}$ (whose real value will be *smaller* than measured). The assumption of a sharp diffusion edge may not be adequate in the shortest L_g devices. Finally, the time dependence of other sequential steps (such as diffusion of H_2 through the $0.5 \mu\text{m}$ thick field oxide, or perhaps some

Figure 8. Temperature dependence of the normalized D_{it} increase during H_2 annealing versus H_2 anneal time. ΔD_{it} is strongly temperature activated. $\tau_{1/2}$ is defined as the time at which ΔD_{it} = half of its normalized value.

hydrogen reactions, etc.), may not be negligibly small in the smallest L_g FETs as assumed.

C. Temperature dependence

To further investigate the time dependence of D_{it} creation during H_2 annealing, the temperature dependence has been determined. Different FETs ($L_g = 1.5 \mu\text{m}$) were FN-injected to $\sim 5 \times 10^{16} \text{ e/cm}^2$. H_2 anneals were performed with $V_g = -5.1 \text{ V}$ at temperatures in the range 278-360K. The resulting *normalized* increase in D_{it} is shown in Fig. 8. The process is clearly strongly temperature activated. An Arrhenius plot of the creation time $\tau_{1/2}$ vs. $1/T$ (K) obtained from the data in Fig. 8 is shown in Fig. 9. Each data point represents data from 2-3 FETs whose τ values typically agreed within $\pm 10\%$. An activation energy E_a of 0.57 eV is obtained from a least-squares fit to these data. Activation energies of 0.45 eV [20] and 0.47 eV [23] have been measured for H_2 diffusivity in bulk silica glass near room temperature. A 0.45 eV activation energy (matched at 295K) is shown in Fig. 9 for comparison. The difference in these activation energies represents a factor of 3.0 difference in τ over the measured temperature range. Although the quality of the data in Fig. 8 is clearly somewhat imperfect (note the abrupt small changes at normalized $\Delta D_{it} \approx 0.9$), it seems unlikely that errors in determining τ could lead to a (relative) factor of 3 error.

Next, experimental values of $\tau_{1/2}$ are compared with calculations from a simple H_2 diffusion model. An approximate diffusion length x may be calculated from $x = \sqrt{(Dt)}$, where D is the H_2 diffusivity ($= 1.4 \times 10^{-11} \text{ cm}^2/\text{s}$ [20]). For a $2 \mu\text{m}$ FET, $x = 0.5 \mu\text{m}$ when the diffusion front has penetrated halfway from the gate edge to the center (note that diffusion occurs from *both* sides of the gate). Thus, time =

Figure 9. Arrhenius plot of D_{it} formation time $\tau_{1/2}$ versus $1000/T$. The experimental activation energy is 0.57 eV. Also shown for comparison (dashed line) is the activation energy for H_2 diffusion in silica glass (0.45 eV).

$x^2/D = 180$ s. Experimentally, $\tau_{1/2} = 1.9 \times 10^3$ s (2.0 μm FET, Fig. 6) which is a factor of about 10 larger than predicted by the diffusion model. Mrstik *et al.* [13] have compared experimental D_{it} buildup times with H_2 diffusion times calculated using a tarnishing model. They find that experimental buildup times are a factor of 10-100 larger than predicted from H_2 diffusion in bulk silica. They attribute the discrepancy to about a 3% densification of thin SiO_2 films grown on crystalline silicon, compared to bulk silica glass. They also observe that compaction should lead to an increase in the H_2 diffusion activation energy. Fishbein *et al.* [22] have measured the annealing of interface traps in hydrogen at 400 - 500°C in poly gate MOS structures. They find that D is about 30 times smaller compared to bulk silica, and the activation energy for H_2 diffusion is larger (0.58 eV). Both observations are in excellent agreement with results here. These results demonstrate convincingly that the time dependence of the D_{it} creation measured here is related to the H_2 diffusion rate.

D. Time-dependent effects

Stahlbush *et al.* [9] have proposed the following model to explain how H_2 annealing after irradiation causes a large D_{it} increase (this model is based on the H^+ model for D_{it} creation after irradiation [1]): (1) Irradiation creates positively-charged defects Q_{ox}^+ in the oxide. (2) During exposure to an H_2 ambient, H_2 diffuses into the oxide. (3) H_2 reacts at Q_{ox}^+ defects to produce positively charge hydrogen ions (H^+) and neutral hydrogen (H^0). (4) H^+ and H^0 drift/diffuse to the Si- SiO_2 interface, where they react to create interface traps.

(Once close enough to the interface, the H^+ ions can pick up an electron, which tunnels from the substrate, to produce H^0 . Thus the actual reaction chemistry at the interface is the same for both H^+ and H^0 .) If $V_g < 0$ during the H_2 anneal, the H^+ ions will drift away from the Si- SiO_2 interface, and cannot contribute to the increase in D_{it} . On the other hand, H^0 motion is independent of the applied bias. Therefore, ΔD_{it} is larger when $V_g > 0$, as is observed in previous H_2 annealing experiments [9-13]. In this work, ΔD_{it} for $V_g < 0$ is about 50% of ΔD_{it} for $V_g > 0$. This ratio is larger than in previous experiments (ratio about ~25%) [9-13]. The reason for this is not understood, but may be associated with (unknown) differences in the oxides studied.

Figure 10. D_{it} growth during H_2 anneal after irradiation for a control oxide and two oxides injected with electrons after irradiation (and before anneal) to remove radiation-induced trapped positive charge Q_{ox}^+ . D_{it} growth is smaller in the injected oxides, which implies that the H_2 reacts with Q_{ox}^+ during D_{it} creation.

In the Stahlbush model, H_2 is cracked by positively-charged defects Q_{ox}^+ remaining after irradiation or FN-stress. Using electron spin resonance, Conley and Lenahan [14] have recently shown that the density of positive E' centers decreases in proportion to the increase in D_{it} (E' defects are radiation or stress-induced hole which are trapped at an oxygen vacancy). This result is strong evidence that the H_2 molecule is cracked at E' centers. In addition, both Stahlbush *et al.* [9] and Mrstik *et al.* [12] have observed that the density of positive oxide charge Q_{ox}^+ decreases roughly in a 1:1 ratio with the D_{it} increase during H_2 annealing experiments. This result strengthens the identification of the E' center as the H_2 cracking site, because E' defects are probably the majority of the radiation-induced positive charge after irradiation. In this work, we also observe a small reduction in Q_{ox}^+ during H_2 annealing after FN-stressing or irradiation (see Fig. 1).

However, the data are not accurate enough to determine whether the ratio is 1:1. The following experiment has been performed to investigate the correlation between post-stress Q_{ox}^+ and D_{it} growth during a subsequent H_2 anneal. After irradiation, several FETs were uniformly injected with electrons at low oxide field (1 MV/cm) using substrate hot electron (SHE) injection [24]. These samples and an un-injected control were then annealed in H_2 with $V_g > 0$ as shown in Fig. 10. Electron injection clearly causes a smaller increase in D_{it} during the subsequent H_2 anneal. Significant electron trapping at low electron injection levels indicates a large trap cross section, which also implies that the trapping defects are probably positively charged. Similarly, a reduced increase in D_{it} was observed in e-injected samples with $V_g < 0$ during the H_2 anneal. Similar results were also obtained for e-injected FN-stressed oxides. It is not surprising that FN-injection results are so similar to irradiation because oxide damage for both types of stress involves holes. In FN-stress, although only electrons are probably injected, holes are created in the oxide by avalanche multiplication [25]. Using a MOSFET carrier separation technique, we find that the ratio of oxide hole current to electron current during FN-injection is about 3×10^{-4} .

One aspect of the experiment in Fig. 10 which remains unclear is why ΔD_{it} continues to fall at the highest ($\approx 10^{18}$ e/cm²) e-injection level. Careful measurements of the threshold voltage shifts as a function of N_{inj} show that essentially all positive charge is removed at $N_{inj} \approx 10^{15}$ e/cm², as would be expected for removal of positive charge with a large capture cross section for electrons ($\approx 10^{-13}$ - 10^{-14} cm²) [25]. Why then does ΔD_{it} continue to fall at higher values of N_{inj} ? It is possible that some of the positive radiation-induced charge is compensated with nearby trapped electrons (similar to the compensation of near-interfacial traps [26]), which would cause the trapped positive charge to appear to have a small cross section.

The cracking reaction of H_2 molecules at stress-induced defects is perhaps the most interesting feature of these experiments, since other processes (H_2 diffusion, H reaction to create D_{it} , etc.) have been studied in some detail previously. This research was undertaken partly in the hope that detailed measurements of the time-dependence could be used to explore this reaction, as attempted by Stahlbush *et al.* [10]. Unfortunately, it now seems clear that the time dependence is determined *primarily* by H_2 diffusion, and not H_2 cracking reaction. There are, however, two instances of time-dependent behavior which are *not* associated with the H_2 diffusion: (1) In Fig. 2, for positive V_g during anneal, ΔD_{it} continues to increase without saturation even at very long times. (2) Studies of ΔD_{it} during H_2 annealing after channel hot carrier (CHC) stress have also been performed on the same FETs used here [15]. In this work, ΔD_{it} increases without saturating to at least 10^6 s. For CHC stress, defects are created in a non-uniform region very close ($\approx 0.2 \mu m$) to the edge of the

drain. From Fig. 6, we estimate the H_2 diffusion time to be relatively small, ≈ 10 -100 s, which appears to be too small to account for the continued D_{it} increase at long times. Qualitatively, ΔD_{it} increases approximately as log(time) at long times in both the CHC data and here in Fig. 2. From these results, we tentatively conclude that this behavior is due to a slow hydrogen-related reaction. Note that this reaction must be different from the H_2 cracking reaction which mostly dominates in this work, and which must be much *faster* than the H_2 diffusion times. Further research is necessary to elucidate the nature of this second hydrogen reaction.

De Schrijver *et al.* have recently observed long-term D_{it} instabilities (increases) in MOSFETs after CHC stress [17]. D_{it} was found to increase approximately as the log(time) up to 10^6 s after stress, and ΔD_{it} is larger for positive compared to negative V_g during anneal. Both of these observations are consistent with CHC results reported in [15]. In both CHC stress papers [15,17], and in this work (Fig. 10) most of the long term D_{it} increase is eliminated with a short electron injection after the stress. This result suggests that the hydrogen reactions involve positively-charged oxide defects. The main difference in these works is that FETs were deliberately exposed to H_2 after stress in [15] and here, so these results must be hydrogen related (essentially no D_{it} increases were observed in unexposed control oxides). On the other hand, results in [17] were not obtained by direct exposure to an H_2 ambient, but rather were found to be associated with the presence of Si_3N_4 passivation layers. The similarity in results suggests that the presence of the passivation layer introduces hydrogen in some form into the gate oxide. Kohler and co-workers [27], among many others, have demonstrated that the radiation and CHC sensitivity of gate oxides can be affected by passivation layers, and that this effect probably arises from hydrogen introduced from the passivation layer. However, the exact source of the log(time) dependence in the CHC experiments is unclear; as discussed above, it cannot be due to simple H_2 diffusion.

In similar experiments, Schwank *et al.* [16] have reported "latent" D_{it} increases at very long times (10^6 s) after irradiation. Hydrogen was not deliberately introduced into these structures, but it could arise from the passivation layers, perhaps due to irradiation. An activation energy of 0.45 eV was obtained for the "latent" D_{it} increase which, as discussed above, is in good agreement with the activation energy of H_2 diffusion in bulk silica glass [20]. Based on this diffusivity, the authors calculate a diffusion distance of $130 \mu m$, which is much larger than the gate length of the MOSFETs ($3 \mu m$). This disagreement is not surprising since, in this work, we measure a time constant for H_2 diffusion of $\approx 10^4$ s at 295K, whereas the time constant of the latent buildup is much longer, $\approx 10^6$ - 10^7 s. Thus, it appears that the rate-limiting step of the latent buildup cannot be due to H_2 diffusion through the gate oxide of the FET. We propose that the rate limiting step could be diffusion of radiation-released H_2 through the

passivation layer. H_2 diffusion through the passivation layer must be slower than in bulk silica glass to account for the results.

SUMMARY AND CONCLUSIONS

D_{it} growth has been measured during H_2 annealing in previously FN-stressed or irradiated oxides. A large D_{it} growth is observed during H_2 exposure, in agreement with several previous reports. This result demonstrates that hydrogen chemistry is involved in the D_{it} creation process. Results from FN-stressed and irradiated samples are almost identical, suggesting the same defects are created by FN stress and irradiation, defects which then react with H_2 during the D_{it} creation process. Experiments using MOSFETs with different gate lengths show that the time dependence of D_{it} growth during H_2 annealing increases rapidly with increasing gate length. This result strongly suggests that the time dependence is determined primarily by "lateral" H_2 diffusion through the gate oxide. This conclusion is supported by the measured activation energy of the time dependence, 0.57 eV, which is consistent with the value for H_2 diffusion in bulk silica glass, 0.45 eV. We argue above that the differences between H_2 diffusion in silica glass and results obtained here are the result of compaction of the thermal gate oxide as proposed by Mrstik [13]. This argument is supported by the excellent agreement between data here and data on H_2 diffusion distance and activation energy (0.57 eV) measured in MOS oxides during a study of D_{it} annealing [22]. Electron injection experiments have been performed after the stress but before the H_2 anneal, which confirm that the H_2 molecules are cracked primarily at positively-charged stress-induced defects. This result is consistent with the spin resonance data of Conley and Lenahan [14] who identify the defect as the well-known E' center. In the case of CHC stress [15,17], and for positive bias at long times, the time dependence cannot be explained by H_2 diffusion, and may be associated instead with slow hydrogen reactions. This case needs further investigation.

It is clear from this work and a number of similar experiments described above that exposure of gate oxides to hydrogen can cause serious reliability problems. In this work, the FETs were deliberately exposed to hydrogen, but in other cases the hydrogen may arise from the passivation layers [16], or even may be liberated from the packaging during irradiation [27]. Our understanding of these effects is still clearly imperfect and bears further investigation. The development and use of improved passivation layers which do not contain hydrogen would also clearly be desirable.

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Figure 11. Schematic diagram of H_2 diffusion from all four sides of the poly gate of a MOSFET.

APPENDIX I. Calculation of 2-dimensional model for H_2 diffusion.

In this appendix, we calculate the characteristic diffusion time $\tau_{1/2}$ using a geometric 2-dimensional model as shown in Fig. 11. In this model, diffusion is assumed to occur from all four sides of the MOSFET gate, as opposed to the simpler 1-dimensional model where diffusion occurs only along the larger dimension. The linear diffusion distance $d(t)$ is assumed at time t which defines an (assumed) abrupt edge to the diffusion region [13]. Using Fig. 11, it is readily shown from geometrical considerations that the *normalized* rate of N_{it} increase is given by:

$$\Delta N_{it} / \Delta N_{it, \max} = (2dW_g + 2dy) / L_g W_g, \quad (1)$$

$$= 2d [1 + (L_g - 2d) / W_g] / L_g, \quad (2)$$

where L_g and W_g are the MOSFET gate length and width, respectively, $\Delta N_{it, \max}$ is the maximum saturated value of N_{it} , and y is defined in Fig. 11. Since, by definition, $\tau_{1/2}$ is the time when $\Delta N_{it} / \Delta N_{it, \max} = 1/2$, by setting Eq. (2) = $1/2$, we obtain a value for d ($\equiv d_{1/2}$):

$$d_{1/2} = W_g / 4 [1 + L_g / W_g - (1 + L_g^2 / W_g^2)^{1/2}]. \quad (3)$$

As a check on Eq. (3), it can be shown that $d_{1/2} = L_g / 4$ in the limit $L_g \ll W_g$ (the range of d is from 0 to $L_g / 2$). Also, $d_{1/2} = W_g / 4$ in the limit as $L_g \gg W_g$. Thus, the 2-dimensional model reduces to the 1-dimensional model in both limits. Finally, since d is a 1-dimensional diffusion distance, d may be expressed as $d = C_1 t^{1/2}$, where C_1 is a constant incorporating the H_2 diffusivity. Consequently, $d_{1/2} = C_1 \tau_{1/2}^{1/2}$. Solving for $\tau_{1/2}$, we obtain:

$$\tau_{1/2} = C_1^{-2} d_{1/2}^2. \quad (4)$$

The relative increase in $\tau_{1/2}$ will be proportional to $d_{1/2}^2$, which can be calculated from Eq. 3 using solely geometric factors.

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