A Mechanism for Enhanced Low-Dose-Rate Sensitivity of Bipolar Transistors

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Abstract—A mechanism for enhanced low dose rate sensitivity (ELDRS) is described in which the key process is the competition between hydrogen creation of interface traps and dimerization. Dimerization dominates at high dose rates, leading to reduced degradation.

Keywords—silicon dioxide, radiation effects, hydrogen radiolysis mechanism, low dose rate effect

I. INTRODUCTION

Ionizing radiation often has a deleterious effect on Si-based microelectronics. For bipolar transistors, the main effect is a reduction in the transistor gain, and this gain reduction has been found to be enhanced as the dose rate is decreased for a given total dose. [1–3] This dependence on dose rate is called enhanced low-dose-rate sensitivity (ELDRS).

The gain reduction occurs because the base current is increased. The primary mechanism appears to be increased carrier recombination at the Si/SiO₂ interface near the emitter-base junction. [4–7] This enhanced recombination is ascribed to an increase in the density of interface traps. For NPN transistors, an additional contribution is the enhancement of the recombination rate of the existing traps. [8] This increased recombination occurs because the electron concentrations at the interface is increased by the electric field arising from positive trapped charge in the oxide overlying the base. [8]

Earlier work on the microscopic mechanisms for ELDRS has not produced a complete explanation. One effort has focused on a mechanism for a dose rate dependence of trapped positive charge. [9] This “space charge” explanation builds on the fact that electrons migrate out of the oxide much more rapidly than the holes. The Coulomb potential of the remaining holes has two effects. One, it hinders the migration of additional holes and thereby reduces the number of holes that are trapped, leading to fixed charge. Two, it hinders the outward migration of electrons and thereby increases the probability that these electrons recombine with trapped holes or compensate the trapped holes by being trapped nearby. This increased recombination reduces the net density of fixed positive charge. In other work, the space charge mechanism has also been used to interpret experiments that measure capacitance to examine the dose rate neutralization of dopants in the Si substrate. [10] The interpretation has been that the protons, ionized hydrogen atoms, are released by the ionizing radiation, and these atoms neutralize some of the dopants in the Si. [10] Another proposed mechanism for ELDRS was inferred to be coupled chemical reactions based on time-dependent data for transistor degradation. [11] In this study, the time-dependent transistor performance was measured during and after irradiation. The data were interpreted in terms of two or more chemical species of unknown origin. [11]

Our report describes a mechanism for ELDRS that follows well-known mechanisms that are incorporated into a computational model to be described. This model incorporates the well-accepted hydrogen mechanism for the creation of interface traps by hydrogen released from sites in the oxide. [12–14] In considering the dose rate effect, an important mechanism in our model is the empirically known reaction of two hydrogen atoms to form hydrogen molecules, a dimerization reaction. [15] A key consequence is that radia-
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tion effects are reduced at high dose rates because an increasingly large fraction of the hydrogen atoms participate in the dimerization reaction instead of defect reactions. In the remainder of the paper the computational model will be described, and this ELDRS mechanism will be illustrated by calculations.

The scope of the paper will be to focus on the essence of the model in explaining the ELDRS effect. As will be discussed, our model is based on a set of defect reactions in the oxide. For completeness, our model includes reactions needed to compute well-known phenomena such as the buildup of trapped positive charge following irradiation. These reactions have been considered in survey calculations to test the computational model and its physical parameters. However, the physical phenomena, such as buildup of trapped charge, and their relation to the reactions will not be described in this report. Furthermore, detailed comparison of the interface trap density to experimental data will not be attempted in this report.

II. The Computational Model

Our computational model attempts to explain the key radiation effects phenomena in silicon dioxide following exposure to ionized radiation. We consider the two main types of effects, the creation of traps at the interface and positive charge in the oxide. Our approach is to develop a computational model whose foundation is the well-known two-step hydrogen radiolysis model. [12] To do this, we define the minimum set of reactions that forms a computable model and estimate the parameters governing these reactions. To estimate parameters, we use electronic structure calculations based on density functional theory [16] together with empirical information and simple approximations based on insight.

The interface traps are assumed to be caused by $P_b$-centers, the well-known defects at the Si-SiO$_2$ interface. These defects are the dangling bonds of Si atoms that failed to bond with the oxide; these dangling bonds can trap carriers that then recombine with carriers of the opposite sign. Thus these defects are also called interface traps. Annealing of $P_b$-centers in a hydrogen environment causes hydrogen to bond to these Si atoms. The resultant $P_bH$ defects are called passivated because they cannot trap carriers. However, atomic hydrogen can react with the passivated defect thereby recreating the original $P_b$ defect. Studies have shown strong evidence that these phenomena are governed by the following exothermic reactions

\[
P_b + H \leftrightarrow P_bH \quad (R1)
\]
\[
P_bH + H \leftrightarrow P_b + H_2. \quad (R2)
\]

The practical result for the semiconductor industry is an annealing procedure which reduces the trap density $[P_b]$ to acceptable levels. The effect of the ionizing radiation, as envisioned in the hydrogen model, is to drive reaction R2 forward. This "depassivation" process produces interface traps, the $P_b$-centers. The model also includes positive charge trapped at oxygen vacancies. These defects may exist in several forms. [18]. The defect of most concern is the $E'$ defect, an oxygen vacancy that has trapped a hole; we denote it by $V_O^-$. This defect is formed by the capture of hole $p$:

\[
V_O + p \leftrightarrow V_O^+. \quad (R3)
\]

At room temperature this reaction can be considered irreversible, thus the trapped holes lead to "permanent" positive charge.

At this point we consider the radiolysis effects of hydrogen. In the two-step hydrogen model, the hydrogen has an important radiolysis effect because it can be released by ionizing radiation and then it can migrate to the interface and de-passivate the $P_b$-center. [12] The radiolytic effects of hydrogen follow after electrons $n$ and holes $p$ are created by ionizing radiation; this process can be written as a reaction in which $R$ represents radiation:

\[
R \to n + p. \quad (R4)
\]

The first stage is the release of hydrogen from a site within the bulk of the oxide. One postulated release mechanism is the capture of a hole at a defect site. [12, 19]

Once released, the second-stage in the model is the migration of the hydrogen to the interface and the de-passivation of the $P_b$-centers. [12] Experiments using electrical bias during the transport stage have led to the conclusion that the transporting hydrogen species is the proton, $H^+$. [12, 20]

Our model builds upon this basic two-stage model by including these reactions as well as other specific reaction that are needed to create a computable model.

We begin by considering a specific source for hydrogen and a release mechanism. Candidate sources include non-bridging oxygen defects and peroxy radicals; however, the source and its release mechanism
are not well-known. Thus we assume a generic defect site $X$ that acts as a source for the hydrogen. The reaction for the assumed formation process is

$$X + H \rightarrow XH.$$ (R5)

Our assumption is that the main conclusions of this work are independent of the details of the hydrogen source or release mechanism.

We assume hydrogen is released in a two-step process. First, a hole is captured:

$$XH + p \rightarrow XH^+.$$ (R6)

Next, the resultant trapped species $XH^+$ dissociates by releasing a proton, $H^+$:

$$XH^+ \rightarrow X + H^+.$$ (R7)

The free protons can migrate to the interface under the influence of the electric field and react with the dangling bond defects.

Conservation of charge is an important consideration in the reactions. At this point we encounter some ambiguity in constructing a model because various charge transfer reactions can be envisioned. For simplicity, we consider only the case in which the proton is neutralized by electron tunneling when it comes near the interface:

$$H^+ (\text{at interface}) + e \rightarrow H.$$ (R8)

An important phenomenon that must be predicted by a model is the effect of hydrogen annealing. In this effect, molecular hydrogen annealing of an oxide containing trapped positive charge leads to the formation of interface traps. These experiments have been interpreted in terms of a mechanism whereby molecular hydrogen is "cracked" to release atomic hydrogen that forms interface states. In our model, this mechanism is included by the reaction

$$V^+ + H_2 \rightarrow V_H + H^+.$$ (R9)

This specific reaction we propose is motivated by electronic structure calculations using QUEST. [16]

Now we focus on reactions that can lead to the dose-rate dependence that is the focus of this report. Thus we consider bimolecular reactions. For example, the direct recombination of electrons and holes must be considered in seeking a dose rate effect. At high carrier density, these could be expected to recombine without causing permanent radiation effects. However, the outflow of electrons is rapid, and thus this contribution can be expected to be small. Another bimolecular reaction, which we find important, is the dimerization of hydrogen:

$$H + H \rightarrow H_2.$$ (R10)

This is a well-known reaction. [15] Our calculations show that the competition of this reaction with reaction R2 can lead to a dose rate effect.

III. FORMALISM

The reactions are incorporated into continuity equations describing reactive transport:

$$\frac{dn_i}{dt} + \nabla \cdot J_i = \sum_j \nu_{ij} R_j.$$ (1)

In this equation, $n_i \equiv n_i(r, t)$ is the density for each species $i$ as a function of position $r$ and time $t$, $J_i$ is the species current density (flux), $R_i$ is the reaction rate, and $\nu_{ij}$ is the stoichiometric coefficient giving the contribution from reaction $j$ to species $i$. [23] In our application of this formalism, the mobile species are electrons $n$, holes $p$, hydrogen molecules $H_2$, neutral hydrogen atoms $H$, and protons $H^+$. Each species contributes to the diffusion current, and the charged species contribute to the convective current. The boundary conditions for the mobile species are set to allow the electrons, holes, molecular hydrogen to flow out of the sample; however, the molecular hydrogen density is assumed to be determined by an external vapor pressure. The atomic hydrogen was not allowed to escape. Poisson's equation is solved to define the time-dependent electric fields governing convective transport. Each reaction contributes forward and reverse terms to the kinetic equations. The reaction coefficients are estimated using transition state theory and simple approximations. Finally, the equations are solved using special techniques to handle the differing time scales of the kinetic phenomena.

IV. RESULTS AND DISCUSSION

The calculations to be described are one-dimensional, time-dependent solutions to the reactive transport equations for an oxide with a thickness of 1 \( \mu m \). The electrons and holes are uniformly injected with a rate $g_0$ for a time duration $t_0$. The initial electron and hole densities are set to be zero. For some species, the total concentration is fixed and independent of time. For example, the total interface trap density, $[P_b]_{\text{total}} = [P_b] + [P_bH]$, remains constant in
Fig. 1. Shows the time-dependent density of various species at the oxide-semiconductor interface during irradiation for a dose rate \( g_0 = 10^{-2} \text{ rad/sec} \) and a duration \( t_0 = 10^4 \text{ sec} \). For this case, the interface trap density rises because of depassivation by hydrogen. The series of reactions triggered by ionizing radiation tends to restore the original source density except for hydrogen that forms hydrogen molecules.

The dependence on dose rate can be seen in Fig. 3 which shows the interface trap density as a function of accumulated dose for the two dose rates shown in Figs. 1 and 2. Clearly, the \( P_b \) density is largest for the lower dose rate.

The dependence of interface trap density \([P_b]\) on dose rate can also be seen in Fig. 4. This figure shows the final trap density reached for each of several calculations for which the total dose is 100 rd(SiO2).
Fig. 3. Shows the interface trap density as a function of total accumulated dose. The low dose rate irradiation leads to larger interface trap density.

This figure shows that the interface trap density becomes independent of dose rate at the lowest rates; however, at the higher rates, the interface trap density decreases with increasing dose rate.

The dose rate dependence shown in Fig. 4 can be understood by examining the reactions. The essence of the mechanism can be understood by examining the two reactions that generate hydrogen molecules as a function of hydrogen density. For this simplified analysis, we assume that the only effect of ionizing radiation is to generate neutral hydrogen at a rate proportional to the dose rate. At low density, which corresponds to low dose rate, the forward portion $k_f(2)[P_bH][H]$ of the harmful reaction, R2, will dominate because it has a linear dependence on hydrogen density whereas the forward portion $k_f(10)[H]^2$ of the harmless dimerization reaction, R10, has a quadratic dependence on hydrogen density. However, as the dose rate and hydrogen density increase, the harmless reaction, R10, will dominate. The domination by the harmless dimerization reaction is the essence of the dose rate effect.

Greater insight can be gained by considering the kinetic equations. This approach is necessary for the more general case we consider in which hydrogen migrates and is allowed to be retrapped at the source. The phenomena can be understood by examining the following approximate kinetic equations:

\[ \frac{d[H]}{dt} = -\nabla J_H + g_H - k_f(2)[P_bH][H] - k_f(5)[X][H] - k_f(10)[H]^2 \]

\[ \frac{d[P_b]}{dt} = k_f(2)[P_bH][H]. \]

The equation for $H$ consists of a migration term $\nabla J_H$, a generation term $g_H$, and the recombination terms. The migration term can be ignored because the gradients are small in the calculations described in this report. The generation term depends on the details of the hydrogen sources; it is proportional to $XH^+$. Using these approximations, the kinetic equation for $H$ leads to an initial transient followed by a steady state solution,

\[ [H]_{ss} \approx \frac{g_H}{k_f(2)[P_bH] + k_f(5)[X] + k_f(10)[H]_{ss}}. \]

Fig. 1 shows that this approximation is very good at low density; Fig. 2 shows that other nonlinear effects start to become important at high density, the high dose rate case.

The time-dependent density $[P_b]$ can now be computed approximately using this steady state solution. The kinetic equation for $P_b$ leads to a density that increases approximately linearly in time following an initial transient because both the $P_bH$ and the $H^0$ densities are approximately constant. Thus,
\[ [P_b(t)] \approx k_f(2)[P_bH][H]_{st}t. \]  

(5)

Figs. 1 and 2 show that this approximation is reasonable but is becoming invalid as the dose rate increases.

This solution can be approximated by inspection in the low and high dose rate limits. In the low dose rate limit,

\[ [P_b(t_0)] \approx \frac{k_f(2)[P_bH]g_Ht_0}{k_f(2)[P_bH] + k_f(5)[X]} \]  

(6)

and thus

\[ [P_b(t_0)] \approx \frac{c_0k_f(2)[P_bH]N_T}{k_f(2)[P_bH] + k_f(5)[X]} \]  

in which the relations \( g_H = c_0g_0 \) and \( N_T = g_0t_0 \) have been used. Thus in this case there is no dose rate dependence. In the high density limit,

\[ [H]_{st} \approx \sqrt{\frac{g_H}{k_f(10)}} \]  

(7)

and thus

\[ [P_b(t_0)] \approx \sqrt{\frac{c_0}{g_0k_f(10)}} k_f(2)[P_bH]N_T. \]  

(8)

This result explains the \( 1/\sqrt{g_0} \) behavior at high dose rate shown in Fig. 4.

An important consequence of our mechanism is that the dose rate dependence shown in Fig. 4 is not universal because its shape depends on parameters that can vary from sample to sample. As can be seen in the reactions, these parameters include the source density \( [X] \), the hydrogenated source density \( [XH] \), and the passivated interface trap density \( [P_bH] \). For example, increasing \( [P_bH] \) tends to shift the dose-rate curve bodily if the \( H \) re-trapping is controlled by the source density. However, if the hydrogen density is instead controlled by the dimerization and by the passivation reactions, then the main effect of increasing \( [P_bH] \) is to extend the low-dose rate region to higher dose rates. Thus one can expect that no dose rate dependence will be seen for certain sets of sample parameters.

An important consideration is the temperature dependence of the mechanism. The effect of temperature on the dose rate effect can be seen in curves shown in Fig 5. These curves show that the increasing the temperature increases the trap density but reduces the dose rate dependence. This can be understood by examining the approximate solutions using the fact that the dimerization reaction is nearly temperature independent. Thus as the temperature increases, the terms \( k_f(2) \) and \( k_f(5) \) in (4) become dominate just as they are in the low dose rate limit. Thus, in this case, increasing the temperature is equivalent to reducing the dose rate.

The overall increase with increasing temperature seen in Fig. 5 arises because the \( k_f(5) \) term becomes dominate for the parameters used in these calculations. If the \( k_f(2) \) term were dominant, then \( [P_b(t_0)] \rightarrow c_0N_T \) at high temperature. The temperature dependence can also be affected by the temperature dependence implicit in the parameter \( c_0 \). In general, the overall temperature dependence may be complicated.

V. Comparison with Data

Before considering data, it is worthwhile to consider some of the limitations of the calculations. Doing calculations to long irradiation times and large total doses is difficult because of computational problems that arise from the differing time scales of the kinetic phenomena. Thus the calculations have not been performed to the realistic irradiation times corresponding to the low dose rates.

Thus the scope of the present study is to describe the essence of the mechanism. Realistic comparison with data will be deferred to a future publication. Thus we rely results from short simulations and we
also ignore the contributions of trapped charge. However, a few simulations to long times have been performed. Also, a few simulations of hydrogen annealing of trapped positive charge have also been done to eliminate unphysical surprises.

Direct comparison with transistor measurements is not attempted in this report; future studies will compare transistor simulations with data. An indirect comparison can be made using the fact that excess base current for PNP transistors is proportional to the change in interface trap density. [7, 25–27] Fig. 6 compares the calculations with excess base current data. [24] Clearly, the general shape agrees with the data if one takes into account that trapped charge and geometrical effects are not considered in our crude comparison with data.

The dependence on sample parameters such as $[P_i H]$, the passivated trap density, as seen in (5), illustrates the fact that our theory predicts that the ELDRS is not universal. This observation is consistent with the fact that ELDRS is not observed in all bipolar transistors. [1–3]

An important consideration is the temperature dependence of the low dose rate effect. This has been studied experimentally for capacitors and transistors. [9, 24] Both studies have suggested that irradiation at an elevated temperature at high dose rates is equivalent to room temperature irradiation at a low dose rate. Fig. 5 suggests that an elevated temperature tends to remove the dose rate dependence. This is consistent with the data. [9, 24] However, it also shows an overall increase, an upward shift of each curve. This effect occurs for two reasons. One, the computed interface trap density does not saturate because the irradiation times are overly short. Two, the numerator and denominator of (6) are controlled by different terms that do not cancel. This follows because the activation energy for interface trap creation ($E_f(2) = 0.5$ eV) is larger than the activation energy for hydrogen recapture ($E_r(5) = 0.25$ eV). Our mechanism may be consistent with the data but further study is needed.

VI. FURTHER DISCUSSION

The effects of an electric field can be expected to be similar to the effects associated with the well-known hydrogen radiolysis model that is the basis for our computational model. [12] In future work the calculations investigating the effects of an electric field will be discussed. The calculations that have been done reveal that the physical parameters such as the trap cross-sections can have a large effect on the qualitative results. The details of the boundary conditions on hydrogen transport may also have a large effect on the results.

The effects of trapped charge and hydrogen annealing have been considered but will not be presented in this report.

The dimerization mechanism can also explain the results of experiments that have shown that irradiation leads to dose rate dependent deactivation of acceptors in MOS capacitors. [10] In our explanation, dimerization reduces the density of atomic hydrogen at high dose rates, and this reduces the deactivation of hydrogen. These results are sensitive to hydrogen transport boundary conditions, and thus a comparison with data will be deferred.

VII. CONCLUSION

In conclusion, we have described a theory of the effects of ionizing radiation on interface traps in microelectronic oxides. From model calculations we have shown that the competition between hydrogen reactions, dimerization and defect formation, can lead to an enhanced low-dose-rate sensitivity (ELDRS) that is consistent with experiments.

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REFERENCES


