A Comprehensive Physically Based Predictive Model for Radiation Damage in MOS Systems

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Abstract

We have developed a comprehensive physically based predictive model for radiation damage in MOS devices. The model involves essentially no adjustable parameter first principles calculations of both oxide hole trapping and interface trap generation. With both oxide positive charges and interface trap generation accounted for, in principle, the model allows calculation of the threshold voltage shifts from processing parameters. The model is based on the statistical mechanics of point defects in solids and extensive electron spin resonance (ESR) measurements of MOS systems. Although we believe that this model is fundamentally correct and that it captures most of the fundamental physics of the damage phenomena, we emphasize that the treatment is first order. The model involves some simplifying assumptions and, in its present form, it applies only to high quality thermally grown oxides. We present the model as a framework for understanding the radiation damage process and as a means to explain a very wide variety of apparently unrelated observations long present in the literature. We believe the approach outlined in this paper will eventually allow manufacturers to build in radiation hard reliability with process design.

I. INTRODUCTION

Although the effects of ionizing radiation on MOS devices have been intensively investigated for over thirty years, no comprehensive physically based predictive models have been developed to describe the process. Such models could provide manufacturers with significant cost savings by allowing radiation hardness reliability to be built into a process with a minimum of build and test iterations.

In this paper we present a comprehensive physically based predictive model for gate oxides. Our use of the word comprehensive is meant to convey that the model covers both primary phenomena in MOS device damage: the generation of positive charge within the oxide and the generation of interface traps at the Si/SiO_2 boundary. Although comprehensive in this sense, we emphasize that the model is a first order treatment.

II. BACKGROUND

Quite a bit is known about the radiation damage process; we utilize the current understanding to develop our model.

The early vacuum ultraviolet irradiation studies of Powell and Derbenwick[1] and Winokur and Sokoloski[2] demonstrated that the damage phenomena results from the presence of holes in the oxide and not from direct photon-defect interactions. Somewhat later studies pioneered by the Harry Diamond group[3-5] convincingly established that the Si/SiO_2 interface trap formation process takes place in two stages: an interaction involving holes in the oxide followed by migration of a (hydrogenic) atomic species to the interface where interface traps are created.

Early electron spin resonance (ESR) studies at Sandia Laboratories demonstrate that two oxygen deficient silicon centers, both involving silicon "dangling bonds" dominate the damage phenomena.[6-10] The radiation induced interface traps are dominated by P_b centers, illustrated in figure 1. The radiation induced hole trapping is dominated by E′ centers, illustrated in figure 2. Although the early ESR studies were at one time quite controversial, the results of the early studies have been confirmed and extended by quite a few independent groups.[11-15]

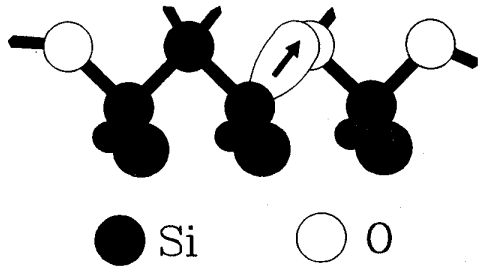

Figure 1: A schematic illustration of the P_{b0} center at a (100) Si/SiO_2 interface.

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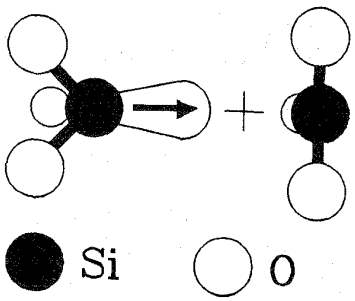

Figure 2: A schematic illustration of an E' center.

The P_b precursor is almost certainly an interface silicon bonded to three silicons and one hydrogen (P_bH). Vacuum annealing studies indicate that the density of P_bH sites would be quite high (~$5x10^{12}/cm^2$).[16] The E′ precursor, at low to moderate ionizing radiation dose, is an oxygen vacancy.

The early Sandia work[7-9] showed that P_b centers have a donor level in the lower part of the Si band-gap, are neutral with the Fermi energy near mid-gap, and have an acceptor level in the upper Si band-gap. Thus, the mid-gap shift in a CV measurement will yield a fairly good estimate of oxide positive charge.[7-9] The early Sandia work showed that the density of generated P_b centers is roughly equal to the number of interface states in the middle half of the silicon band-gap.[6-10]

Some time ago, Kohler etal[17] showed that radiation induced interface trap generation was significantly increased if a device were to be irradiated in an ambient containing H_2. Several later studies showed that post irradiation H_2 exposure also resulted in a significant additional increase in interface trap formation.[18,19]

Recently, we showed that MOS oxide E′ centers react at room temperature with molecular hydrogen on the same time scale at which (P_b center) interface trap generation occurs.[20,21] Significant quantities of radiolytic atomic hydrogen are created in MOS oxides subjected to ionizing radiation.[22] At room temperature, this atomic hydrogen is almost instantly dimerized to form H_2. Therefore, in an MOS device irradiated at room temperature, we would find E′ centers, P_bH centers, and H_2 during and immediately after irradiation. The capture of a hole at the E′ site opens up the defect site as illustrated in figure 3. With the hole capture event, a reactive silicon dangling bond site is created in the oxide. It is the interaction between this reactive dangling bond in the oxide with the passivated (P_bH) dangling bonds at the Si/SiO_2 boundary and with molecular hydrogen which provide the basis for the interface state formation part of our model. Our comprehensive model is based upon these three entities and upon the understanding that E′ centers react spontaneously with molecular hydrogen at room temperature. In developing this model we have used what we know about these three entities and made the simplest assumptions about the statistical mechanics and chemical reactions.

III. THE MODEL

Last year at this meeting we presented a physically based predictive model of oxide hole trapping.[23,24] It was based upon the statistical thermodynamics of point defects in solids and upon our knowledge of E′ centers. In this study, we combine that model with a new model for interface trap formation based upon the E′ centers, P_bH and P_b centers and molecular hydrogen.[25] As was the case for the oxide hole trap model, this model is based upon ESR results and the statistical thermodynamics of solids.

A. Statistical Mechanics of Solids

The basic principle in our calculation is that, at constant temperature and pressure, a system reaches equilibrium when the Gibb's free energy, G, is minimized. The Gibb's free energy is given by

$$G = H - T S, \tag{1}$$

where H is enthalpy, T is absolute temperature, and S is entropy. The enthalpy is the sum of internal energy, E and the product of pressure and volume, PV.

B. Oxide Hole Traps and E′ Precursors

For E′ center precursors, the minimization of Gibb's free energy yields[23,24]

$$n = Ne^{\Delta s_f/k - \Delta h_f/kT}, \tag{2}$$

where n is the number of E′ center precursors and Δs_f represents the (large) nonconfigurational entropy per defect, Δs_f the formation enthalpy per defect, k is the Boltzmann constant, T is the temperature at which equilibrium is reached, and N is the number of available sites.

The standard expression for charge capture versus fluence for an insulating film is[26]

$$N_t = N_o(1 - e^{-\sigma\eta}), \tag{3}$$

where N_t is the density of trapped charges, N_o is the total number of traps, σ is the capture cross section, and η is the fluence, that is, the number of holes/cm^2 which cross the

oxide. (A detailed discussion of charge trapping expressions is provided in reference #26.)

Combining expressions (2) and (3) with our knowledge of the E′ center capture cross section at moderate electric field strength, $\sigma \simeq 3 \times 10^{-14}$ cm^2, and a measurement of E′ center precursor formation enthalpy, $\Delta h_f \simeq 1.5 \pm 0.1$eV, we developed an expression for the mid-gap shift of an oxide, ΔV_{mg}, subjected to a hole fluence η:

$$\Delta V_{mg} = \left\{ \frac{qN e^{\Delta s_f / k} e^{-\Delta h_f / kT}}{C_{ox}} \right\} \left(1 - e^{-\sigma\eta}\right), \qquad (4)$$

where q is electronic charge, and C_{ox} is the oxide capacitance per unit area. The mid-gap shift, the CV shift corresponding to the Fermi level at mid-gap is a fairly good measure of oxide positive charge.[7-9]

As we have pointed out in our earlier publications[23,24] dealing with the hole capture model, expression (4) is based on two assumptions. (1) The system comes reasonably close to equilibrium defect density at the given temperature T. (2) The cooling rate down from this temperature is sufficiently rapid so as to "quench" in that defect density. Although we believe these assumptions are reasonable for the discussions presented herein, it is important to realize that a finite period of time is required to achieve these equilibrium values. We have conducted a preliminary study of the approach to equilibrium for both E′ center precursors and the oxide hole traps.[27] We grew oxides at 875 °C and subjected them to rapid thermal anneals at 950, 1050, and 1100 °C. Our preliminary results indicate that the time required to reach a saturation or equilibrium value for both E′ precursors and hole traps is strongly temperature dependent: ~ 10^2 sec. at 1100 °C and considerably longer, ~10^3 sec. at 950 °C. Although these results indicate that our assumptions are reasonable for the discussions contained herein, they also illustrate the necessity of a kinetics component for application of this model to relatively low temperature processing.

C. *Interface Traps, P_b, P_bH, E′ and H_2*

Expression (4) provides an estimate of the mid-gap CV shift. A more useful expression would be the threshold voltage shift, ΔV_{th}, which would include, for an n-channel device, negative space charge from P_b centers, and compensating positive charge from the E′ centers.

To predict ΔV_{th} we must be able to predict the density of positively charged oxide E′ centers, as well as the density of Si/SiO_2 interface P_b centers and be able to approximate of the P_b center's density of states.

The approximate P_b density of states has been known for some time. It was approximately determined as a result of measurements of P_b paramagnetism versus the Si/SiO_2 interface Fermi energy (see figure 3).[7-9] The P_b centers have two broad levels in the Si band-gap. As the Fermi level moves from low in the gap to about mid-gap, P_b centers accept one electron and become electrically neutral. As the Fermi level advances from near mid-gap to the conduction band edge, the centers accept a second electron and become negatively charged.[7-9] As figure 3 indicates, in an n-channel device, the substantial majority of P_b centers will be negatively charged at the threshold voltage; thus, their contribution to the threshold voltage will be

$$\Delta V_{th}(P_b) \simeq \frac{e[P_b]}{C_{ox}}, \qquad (5)$$

where $[P_b]$ is the density of centers per unit area.

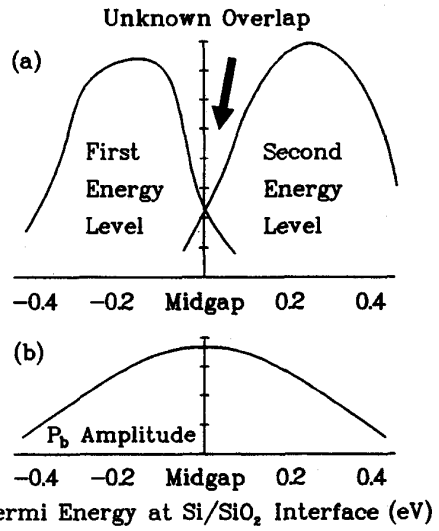

Figure 3: In (a) we illustrate the approximate P_b center density of states obtained from the P_b paramagnetism versus Fermi energy response sketched in (b).

If we assume that P_b generation proceeds via Si - H bond breaking and we recognize that H_2/E′ reactions occur spontaneously at room temperature, we expect that the reaction would necessarily be of the form

$$\alpha H_2 + \beta P_b H + \delta E' \rightleftarrows \Phi H_2 + \gamma P_b + \mu E'H. \qquad (6a)$$

The right and left sides of this expression must equal one another; that is, the number of hydrogens, number of E′ sites etc. must be the same on both sides. So, $\delta = \mu$; $\beta = \gamma$. Since an E′ hydrogen reaction corresponds to a P_bH depassivation, $\mu = \beta$ and thus $\mu = \beta = \delta = \gamma$. The number of hydrogens on both sides of the expression must also balance, so $2\alpha + \beta = 2\Phi + \mu$, thus $\alpha = \Phi$. If we divide both sides of (6a) by μ and call $\alpha/\mu = \Phi/\mu = \lambda$, we obtain

$$\lambda H_2 + P_bH + E' \rightleftarrows \lambda H_2 + P_b + E'H. \qquad (6b)$$

We expect that reaction (6) would proceed significantly toward completion during or immediately after a device is exposed to ionizing radiation. This is so because elementary statistical mechanics tells us that, if this system were to reach equilibrium,[28]

$$\frac{[P_b][E'H]}{[P_bH][E']} = \exp\left(\frac{-\Delta G}{kT}\right) = K, \qquad (7)$$

where ΔG represents the difference in Gibb's free energies of reactants and products. We would expect that the change in the Gibb's free energy would be relatively small because in this reaction a hydrogen atom is transferred from a silicon atom at the Si/SiO_2 boundary to a silicon atom in the oxide. This transfer would presumably involve only a small change in enthalpy. Thus, K would be at least within about an order of magnitude of one. This means that the reaction would proceed significantly towards completion. Note that kinetics is not an obstacle here. We earlier reported E′/H reactions at room temperature on the same time scale as interface trap generation.[20,21]

Consider the technologically irrelevant but interesting case in which a very poor device with a high initial interface trap density is subjected to irradiation. Equation (6) indicates that, in this case, with very few P_bH sites available, the reaction would be driven to the left. In this case, the interface trap density would decrease with exposure to ionizing radiation.

Now consider the technologically important case in which the initial conditions involve very high P_bH concentration and very low P_b concentration. To solve expression (7) for ΔP_b, the concentration of P_b centers generated by ionizing radiation, we define an initial, pre-irradiation P_b density to be P_{bi}, an initial pre-irradiation P_bH density to be $(P_bH)_i$ (about $5x10^{12}/cm^2$) and the density of E′ centers present immediately after irradiation and after all the holes not trapped are swept from the oxide, to be E'_i. (For simplicity of discussion and calculation, we consider a device subjected to a brief burst of ionizing radiation.) We also take the number of E′H complex sites to be equal to the number of P_b sites created. With these terms defined, expression (7) can be written as

$$\frac{[P_{bi} + \Delta P_b][\Delta P_b]}{[(P_bH)_i - \Delta P_b][E'_i - \Delta P_b]} = K. \qquad (8)$$

For the technologically important case in which the initial pre-irradiation Si/SiO_2 boundary has a very low interface trap density, $P_{bi} \sim 0$. For a low dose, that is, for $\Delta P_b << (P_bH)_i$, expression (8) becomes

$$\frac{[\Delta P_b][\Delta P_b]}{(P_bH)_i (E'_i - \Delta P_b)} = K. \qquad (9)$$

For a relatively low dose, then, our model yields

$$\Delta P_b \approx K/2\,(P_bH)_i\left\{(1 + 4\,E'_i/[K(P_bH)_i])^{1/2} - 1)\right\}. \qquad (10)$$

A qualitative understanding of our model may be gleaned from a consideration of expression (1). The configurational entropy will increase with the transfer of hydrogen from the uniformly "filled" P_bH sites to the uniformly "empty" E′ sites. Note that molecular hydrogen is not created or consumed in this process if all the initial P_b sites are occupied by hydrogens. Thus, in devices which initially have low interface trap density, molecular hydrogen effectively plays the role of catalyst. Note also that the reaction will not necessarily proceed all the way to the equilibrium concentration. Hydrogen molecules have an extremely high diffusion constant in SiO_2 and will quite rapidly be dissipated. Also note that, particularly in a dry oxide, the radiolytic hydrogen generated may be inadequate to allow the reaction to proceed close to equilibrium.

Before discussing the literature in terms of this model, a brief discussion of some aspects of the statistical mechanics may prove useful.

The configurational entropy change in the system could be calculated from

$$\Delta S_c = k \ln \Omega, \qquad (11)$$

where k is the Boltzmann constant and Ω represents the number of distinct ways in which these atoms may be arranged. If we initially have N_1 P_bH sites and N_2 E′ sites, with all potential P_b sites occupied by hydrogen, removing one hydrogen and placing it on an E′ site would lead to $\Omega_1 = N_1N_2$ distinct arrangements. Thus,

$$\Delta S_{c1} = k \ln(N_1N_2). \qquad (12)$$

Since $\Delta G = \Delta H - T\Delta S$, if N_1 and N_2 are large, the process is inevitably thermodynamically favorable. ($kT \simeq 0.025$ eV at room temperature.)

A second transfer is almost as thermodynamically favorable; the first hydrogen leaves only $(N_2\text{-}1)$ remaining E′ sites available for the second. Only $(N_1\text{-}1)$ possible P_bH sites can now lose a hydrogen. Since the hydrogen empty P_b sites and hydrogen filled E′H sites are, in each case, indistinguishable from one another, $\Omega_2 = N_1(N_1 - 1)N_2(N_2 - 1)/2x2$. The process is easily extended to the transfer of an arbitrary number of hydrogens, n. ($\Omega_n = N_1!N_2!/(N_1 - n)!(N_2 - n)!(n!)^2$.)

The point here is that the process proposed in our model inevitably occurs to some extent if kinetics allows it. Since the change in enthalpy associated with moving a hydrogen atom from a silicon at the interface to a silicon in the oxide is small, the reaction constant K should be fairly large, at least within an order of magnitude or so of one. Since we observe E'/H_2 reactions occurring over short time spans (minutes) at

room temperature, we know that kinetics does allow this process.

On the basis of vacuum annealing experiments, the density of P_bH sites is about $5x10^{12}/cm^2$.[16] Expression (10), which we take to be a reasonable approximation at low dose levels is relatively insensitive to the $(P_bH)_i$ value so this rough estimate is adequate for the purposes of our discussion. Expression (10) also yields a result which changes slowly with changes in the equilibrium constant K. Therefore, our preliminary estimate that K is within an order of magnitude or so of one is also adequate for the purposes of semiquantitative discussion.

We thus have a first order model which incorporates both oxide hole trapping and interface trap generation. We believe this model captures most of the fundamental physics of the radiation damage process and that it explains a great deal of apparently unrelated observations in the literature. We do not however believe that this model is complete or perfect.

D. Gate Bias Dependence and the McLean Model

Our expression (10) does not have any explicit bias dependence. However, our model does implicitly involve transport of some hydrogenic species between the oxide hole trap and the interface trap formation site.

Extensive kinetic studies pioneered at the Harry Diamond Laboratory,[2-5] later refined and extended by work at NRL,[29] can be explained quite well by the proton transport model of McLean.[5]

Although our model does not specifically address the details of the McLean Model, it is consistent with it. In view of the strong experimental evidence which supports this model, we interpret our expression (10) to correspond to the eventual P_b concentration generated under significant positive bias and provisionally assume that the positive bias is required for reasons discussed by McLean,[5] that the positive bias drives the protons towards the Si/SiO_2 boundary.

IV. LIMTATIONS OF THE MODEL

The model has several limitations with regard to its treatment of E′ centers. Although quite a few studies have established that E′ centers dominate oxide hole trapping in a wide variety of oxides,[9-16] the modest precision of ESR measurements do not allow us to say that all oxide hole trapping is due to E′ centers. (It's worth mentioning also that in some oxides E′ centers do not dominate hole trapping.[30]) At least three E′ variants have been identified in thermally grown oxides. Although one center, the generic E′ defect, generally appears to dominate, two other variants can play significant roles in hole trapping.[30] Although differences in hole trap capture cross sections and in hydrogen/ E′ reactions are not large, our treatment of all the centers as a single defect must be viewed as only an approximation.

Another limitation regarding the E′ density computation involves the observation that in some oxides considerable compensation exists between positive and negative charge. As we discussed in an earlier publication,[24] compensation effects would require multiplying the actual E′ densities by a factor of order one.[31]

The most serious limitation of our treatment and, in our view, the most serious gap in the current materials related literature on basic mechanisms is the lack of a detailed quantitative description of the relationship between the concentration of hydrogen at various bonding sites and radiation response. Specifically with regards to our model, the most serious hydrogen bonding chemistry limitation is the model's neglect of structural changes at E′H sites which clearly occur; for example, the creation of the 74 Gauss doublet and 10.4 Gauss doublet hydrogen complexed E′ sites must involve fairly complex structural rearrangements at these sites.[20,21] Another aspect of this problem is the possibility of neutralization and recharging of E′ sites.

At the present time, we do not know if structural changes at the E′ sites might include the eventual loss of the hydrogen and the possible regeneration of the original E′ precursor or some other E′ variant which could then take part in additional interface trap generation. (Preliminary results suggest reduced stability of E′ hydrogen complexes.)

Although not precisely a model limitation, a limitation of our current treatment is the modest range of process parameters over which we have calibrated equation (2).[23,24] Since an enthalpy of creation is the result of a defect reaction and since one defect may, at least in principle, participate in more than one reaction, it is possible that our $\Delta h_f \sim 1.5$ eV will not be appropriate for all processing conditions.

Nevertheless, we believe that our model captures enough of the fundamental physics of the damage process so that, even in its current form, it is predictive. The model explains quite a few apparently unrelated observations in the literature.

V. MODEL PREDICTIONS: COMPARISONS WITH RESULTS IN THE LITERATURE

(1) As mentioned earlier, our model predicts that a radiation induced decrease in P_b density would occur if device structures with high initial P_b density were subjected to ionizing radiation. It thus also predicts a radiation induced decrease in interface state density if devices with high initial interface state density are subjected to ionizing radiation. Awazu etal[15] have studied the effects of ionizing radiation on Si/SiO_2 structures with high initial P_b density. As our model predicts, they observed a radiation induced decrease in P_b density. Milanowski etal[32] have variously stressed MOS devices and also observe a decrease in interface trap density if the initial interface trap density is high.

(2) Our model's equation (10) predicts that, if a good oxide were to be flooded with a small number of holes, the initial trapped hole density would be about equal to the number of interface traps generated (Actually, since each P_b

has two levels, the ratio would be two interface states per trapped hole.)

Many years ago, Hu and Johnson[33] flooded oxides with a small number of holes, via x-ray irradiation, at temperature low enough to suppress interface trap generation. Measuring initial hole concentration and then allowing the interface trap generation to proceed, they observed an approximately one to one correlation between the initial hole density and the final interface trap density.

(3) Our models (zero or first order) predictions for generated interface state density are independent of the location of the hole trapping. (We don't specify the intermediate hydrogen species traveling between the E'/E'H site and the P_bH/P_b site, but assume this species is sufficiently long lived to allow the reaction to proceed, the predicted P_b generation is therefore independent of the location of the E' center sites.)

Linear accelerator (LINAC) studies of the radiation damage process have shown that devices briefly irradiated under positive or negative gate polarity exhibit approximately equal eventual interface trap densities provided that the bias is, in both cases, positive immediately after irradiation.[3,4] At least for polysilicon gate devices subjected to a high temperature post poly anneal, one would expect about equal density of E' precursors on both sides of the oxide. Thus about equal densities of E' centers would be "activated" by hole trapping in each bias polarity. With about the same number of E' centers generated, the model predicts that, as observed, about the same number of interface traps would eventually be generated for both polarities.

(4) Since our model involves the interaction of a trapped hole E' site with molecular hydrogen as the trigger for interface trap generation, one would expect that in the LINAC experiments discussed in (3) a longer time would be required to build up the interface traps in the negative bias case. This behavior is observed.

(5) Our model predicts that interface trap generation would be sublinear in dose at moderate to high dose. It also predicts that, to a good approximation, the interface trap generation would be linear in dose at low total dose. In addition, the model predicts that the linear response which would extend over a wider range of dose in a hard oxide than in a soft oxide and would extend to higher dose in thinner oxides than in thick oxides. These predictions are consistent with a very large number of observations in the literature.[34-41]

The linear-sublinear interface state generation response results because, as expression (3) indicates, E'_i is also sublinear in dose. At low dose, of course, both expressions (3) and (10) can be expanded to linear expressions, since for small x, $e^x \approx 1 + x$ and $(1 + x)^{1/2} \approx 1 + x/2$. Thus the exponential of expression (3) may be expanded as $\exp(-\sigma\eta) \sim 1 - \sigma\eta$, if $\sigma\eta << 1$, yielding a low dose initial trapped hole density of $N_o\sigma\eta$. If the ratio of initial trapped hole density to initial P_bH density is sufficiently low, then the square root term of expression (10) could be expanded to $1 + 2E'_i / [K(P_bH)_i]$, thus yielding a linear rate of interface trap generation if the hole trapping is also linear.

For a given dose, the fluence η is approximately proportional to oxide thickness; thus, E'_i vs. dose would be linear to higher dose in thinner oxides. The N_0 parameter is large in a soft oxide, small in a hard oxide; so, if one were to compare linear versus non-linear response in hard and soft oxides of equal thickness, one would expect the softer oxide to deviate from linearity at lower dose.

The model's predictions are consistent with quite a few studies in the literature. Many studies have reported a sublinear dose dependence of interface state generation, mostly on relatively thick oxides at moderate to relatively high dose.[34-39] At quite low dose a linear dose dependence is reported.[40] In very thin oxides a linear dose dependence is observed.[41]

Benedetto etal.[42] have compared relatively hard and relatively soft MOS devices with identical oxide thickness and find that the soft oxides exhibit sublinear ($\sim(\text{dose})^{1/2}$) dose dependence of interface trap generation and that the harder oxides exhibit a linear response at moderate dose levels.

(6) Our model predicts that the interface trap densities generated will be strongly correlated with the density of trapped holes and that, at moderate dose levels, these densities will be of the same magnitude. Ohnishi[43] has compared trapped hole and interface trap generation in MOS oxides grown over a range of process parameters and then irradiated to 1Mrad (Si). Some oxides were grown at 1000 °C others at 1100 °C; oxides were grown in a dry O_2 diluted with N_2 and Ar. In all cases, the interface traps and trapped hole densities were strongly correlated.

(7) Radiolytic molecular hydrogen will be quite rapidly dissipated because its diffusion coefficient in SiO_2 is quite high. Thus, in at least some devices, one would expect that the equilibrium values of P_b would never be reached. One would thus expect that post irradiation exposure to an H_2 rich ambient would cause an additional increase in interface trap density. This behavior is observed.[18-19,21]

(8) Since E' center precursor density increases exponentially with increasing processing temperature, one would expect that a similar increase in generated P_b would also occur. This has been observed.[10]

(9) Our model is consistent with analysis of results of bias annealing of oxide trapped holes[44] which show that the dominating deep hole traps have quite deep levels, below the silicon valence band edge. Our model's dominating deep hole traps are E' centers; as a result of computational studies[45], it has been known for some time that E' centers have a deep level around the middle of the SiO_2 band-gap.

In addition, our model is at least qualitatively consistent with a more detailed analysis of bias annealing results which indicate a broader distribution of hole traps in soft oxides than in hard oxides.[44] (This broader distribution of E' centers in soft oxides is also strongly suggested by spin dependent recombination studies.[46,47])

In our model, the E′ density is proportional to $\exp(-\Delta h_f/kT)$, where, as we have discussed previously,[23,24] Δh_f can be reduced by strain energy release. According to Omameuda[48], this strain energy could be in the range of several tenths of an electron volt very near the Si/SiO_2 boundary. Thus, very near the Si/SiO_2 interface, the trap density would be higher than the trap density further into the oxide, because the activation energy close to the Si/SiO_2 boundary would be lower there. Although this would be so for all temperatures, the relative fraction of near interface to "bulk" oxide trap densities would diminish as the temperature is increased. Thus, a soft oxide (exposed to higher temperature) would inevitably have a broader hole trap distribution than a hard oxide (exposed to a lower temperature).

(10) Our model is consistent with studies of radiation damage in thin and very thin oxides which show that both hole trapping and interface trap generation drop to near negligible levels for oxides < 50 Å.[41,49,50]

Our model requires that a hole be captured at an E′ site to trigger interface trap generation. The hole "opens up" the E′ site and creates a silicon "dangling bond" in the oxide which then can react with hydrogen.

In a very thin oxide, electrons tunnel in to the E′ trapped hole site annihilating the positive charge and removing the "dangling bond" before the hydrogen reaction can take place. Thus our model would predict that at the approximate thickness at which trapped hole buildup ceases, interface trap formation would also cease. More precisely, our model predicts that if the oxide is sufficiently thin so that the trapped oxide charge is essentially all annihilated by tunneling before the hydrogen reaction occurs, no interface trap formation will occur.

Our model allows a rough, at least semiquantitative, estimate of the oxide thickness at which the interface trap formation and hole trapping would disappear. We know that the interface trap formation process proceeds over a period of many seconds and that the generation process is most rapid during the first few seconds. For the purpose of this semiquantitative argument, consider a period of one to ten seconds. Using a mid - SiO_2 band-gap E′ level (E_t = 4.5eV) and a simple tunneling calculation[51], one would expect that E' sites within a distance x of an Si/SiO_2 interface would lose their positive charge to a tunneling electron at a rate given by an attempt frequency ν times a tunneling transmission coefficient T. Manzini and Modelli argue that $\nu = 10^{13}$/sec.[52]

Ignoring the oxide electric field, one would obtain a rate R given by

$$R = \nu T = (10^{+13}/\text{sec})\exp\left\{ -\frac{(32m)^{1/2}\pi (E_t^{1/2}x)}{h} \right\}. \quad (13)$$

If we take m to be 0.4 times the electron mass, a result used in other oxide tunneling studies[52], R ≈ 0.1 to 1 sec^{-1} for x ≈ 21 to 24 Å; thus our crude calculation indicates that both hole trapping and interface trap generation would be reduced to negligible levels for oxides thinner than about 50 Å, a prediction reasonably consistent with the experimental results.[41,49,50]

(11) Our model is consistent with thermally stimulated current (TSC) measurements of both Shanfield etal.[53] and Fleetwood etal.[31] in that quite similar TSC spectra are observed for quite a wide range of oxides, a strong peak near ≈ 1.8 eV with a broad shoulder extending down to ≈ 1.2 eV. Our model has one dominating deep hole trap defect for a wide range of oxides, E′ centers. The TSC results indicate one type of TSC spectrum for a wide range of oxides, a result consistent with one dominating variety of oxide hole trap defect.

Furthermore, some analysis of our model's specific dominating hole traps, E′ centers, provide a straightforward explanation for the apparent discrepancy between the relatively shallow hole trap depth measured in TSC (~ 1.2 - 1.8 eV) and the much deeper trap depth extracted from tunneling studies like those of Oldham etal.[44] Quite a large structural change takes place upon hole capture at E′ sites. Thus, due to the Franck-Condon principle,[54,55] E′ sites would produce a deep tunneling or optical trap but a considerably shallower thermal trap.

(12) Our model is also consistent with results and conclusions of an extensive study by the Sandia group[56] which showed a striking correlation between the oxide field dependence of hole trapping and interface trap generation. As a result of their observations, Shaneyfelt etal.[56] proposed a direct link between hole trapping hydrogen interactions and interface trap generation. Both results and conclusions of this earlier Sandia work are consistent with the model proposed herein.

(13) Our model for interface trap generation requires the system to approach equilibrium after irradiation, thus, if a significant bias is maintained during irradiation (and E′ trapped holes are not permitted to recombine with electrons in the oxide) the model is dose rate independent. This behavior is observed.[57] (With a very low oxide electric field present, one would expect repeated electron hole recombination at E′ sites; it's not clear to us what this model would predict under these circumstances.)

VI. HYDROGEN

Assuming that the fundamental ideas in the model are correct, its most serious shortcoming is its qualitative and uncalibrated treatment of hydrogen. At the present time, to the best of our knowledge, no detailed studies of the relationship between the concentration and location of oxide hydrogen and radiation response have been carried out. Recent Fourier transformation infrared spectroscopy (FTIR) studies (not involving radiation damage) have clearly demonstrated the sensitivity and analytical power to identify both the concentration and chemical buildup of hydrogen in SiO_2 films on silicon.[58,59] We believe FTIR studies of processing effects on radiation response would be extremely

useful in developing a more complete understanding of the radiation damage phenomena, as well as improving the predictive power of this (or other) physically based predictive models of radiation damage.

VII. A Dissenting Opinion About P_b Center Structure And Electronic Properties

It should probably be noted that one important aspect of our model is somewhat controversial. Our model involves two basic ideas about P_b centers: (1) that they are dominating interface state defects and (2) that they are interface silicon dangling bond defects. Both of these ideas are supported by studies of quite a few groups.[6-10,13-15,60-63] However, one group, Stathis and coworkers, have strenuously objected to both of these basic ideas about P_b centers.

On the technologically important (100) Si/SiO_2 interface, the P_{bo} center variant dominates.[13,60] Stathis and Dori[64] argue that "the defect responsible for the P_{bo} resonance either is fundamentally different from a dangling bond or lies deeper inside the silicon away from the interface." Recently Cartier and Stathis[65] wrote that "prior to these studies, it was widely accepted that the silicon dangling bond defect, which gives rise to the well known P_b signal in electron spin resonance (ESR) is the microscopic defect causing the fast interface state. As will be outlined in this contribution, we cannot support this view." They go on to argue that, "silicon dangling bonds, as detected by ESR measurements, account for only a small fraction of the electrically detected interface states."

Cartier and Stathis draw their conclusions with respect to the P_b center's role in interface states upon studies in which they bombard $Si/Si0_2$ structures with ***extremely*** high fluences of atomic hydrogen (up to 10^{21} hydrogen atoms/cm^2) to generate extremely high densities of interface states ($> 5 \times 10^{12}$/cm^{2}eV). There are quite a few problems with the Cartier/Stathis study. At least five bear mentioning.

(1) The $\approx 10^{21}$ hydrogen atoms/cm^2 used in their study corresponds to about *one million monolayers*. A typical oxide ~ 100 Å thick with ~ 0.1 atomic percent hydrogen would have about 10^{14} hydrogen atoms/cm^2. Thus, the amount of hydrogen involved in their model experiments is many orders of magnitude greater than that present in the process they are attempting to model.

(2) Atomic hydrogen is dimerized in a fraction of a second at room temperature.[66] At room temperature, generation of interface states proceeds for *many seconds* after a device is exposed to ionizing radiation.[3-5] Since atomic hydrogen is not present during nearly all the time involved in interface state generation, atomic hydrogen by itself *cannot* be responsible for most of the process.

(3) Johnson etal.[67] have shown that atomic hydrogen is extremely effective in annihilating silicon dangling bonds. Testing a silicon dangling bond generation model with a process known to annihilate silicon dangling bonds is, at best, a questionable approach.

(4) A fourth problem with the work of Stathis etal. involves the extremely high amounts of energy which would be required to generate fluences of 10^{21} hydrogen atoms/cm^2. For example, if one were actually to flood an interface with 10^{21} hydrogen atoms/cm^2 say via ionizing irradiation, one would necessarily have to break 10^{21} hydrogen atom bonds/cm^2. If each bond energy is ~ 2 eV, ~ 2×10^{21} eV/cm^2 would be absorbed by the ~ 100 Å oxide involved. (Stathis etal. reported results of P_b generation in 97.5 Å oxides.) One rad = 10^2 ergs/gram. For $Si0_2$ then, 1 rad = 1.4×10^{14} eV/cm^3. Thus, for a 100 Å thick oxide, a fluence of 10^{21} hydrogen atoms/cm^2 would correspond to a dose of *at least* 1.3×10^{13} rads. This is about a million times higher dose level than the highest levels utilized in the earlier studies and, not coincidentally, a million times higher than the upper limit of technological relevance. Indeed, this amount of energy is orders of magnitude higher than that required to *vaporize* the oxide sample in question.

(5) The fundamental Stathis/Cartier result, gross differences in P_b and interface state densities, involved EPR measurements of P_b centers on 97Å oxides and capacitance versus voltage measurements on 495 Å oxides.[68] Studies of radiation damage have consistently shown that interface state generation is a very strong function of oxide thickness.[41,49,50,69] Since very large differences in interface state generation are consistently observed for different oxide thicknesses, one would not expect a 97Å oxide and a 495 Å oxide to exhibit comparable interface state densities in the process which Cartier and Stathis attempt to model.

Stathis and Dori draw their conclusions with respect to P_{b0} center structure on the basis of some rather limited annealing studies. In our opinion, the evidence is that P_{b0} centers are indeed Si/SiO_2 interface dangling bonds is overwhelming; however, this evidence involves analysis of ESR g-tensor and hyperfine tensor data.[61-63] This evidence and analysis is fairly detailed and inappropriate for this publication. A review and analysis of this evidence has recently been published elsewhere.[70]

VIII. Conclusions

We have developed a first order comprehensive model for radiation damage in MOS devices. The model is comprehensive in the sense that it predicts both interface trap generation and oxide hole trapping. The model presents a unified explanation for quite a few apparently unrelated observations in the literature.[1,2,6-27,29-44,46-50,52-57,60,69,70]

Although our model is clearly a first order treatment and is clearly subject to several limitations in its present form, we believe our approach will eventually provide manufacturers with significant cost savings by allowing radiation hardness reliability to be built into a process with a minimum of buildup and test iterations.

IX. ACKNOWLEDGEMENT

Work done at PSU was supported by Dynamics Research Corporation.

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