Quantitative Model of Radiation Induced Charge Trapping in SiO_2

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Abstract

A predictive model of radiation induced oxide charging, based on statistical thermodynamics and electron spin resonance measurements of defects known as E' centers, has been developed. The model is successfully tested on ^{60}Co irradiated MOSFETs.

I. INTRODUCTION

The rad-hard community has begun to adopt from the commercial microelectronics industry the growing movement that is known as building in reliability (BIR) [1,2]. The idea behind BIR is to establish a physical understanding of the links between variations in process parameters and future radiation failure mechanisms. One might then use this understanding to adjust the appropriate process parameters to achieve an arbitrary level of radiation hardness with a minimum of performance tradeoffs. The prospects of savings in development time and costs, of avoiding radiation testing, and the advantages of using a commercial foundry to build small lots of rad hard parts is quite enticing. Before any of this can come to pass, however, one must first develop physically based models [3] of the effects of process variables on radiation hardness. Despite nearly 30 years of intense study, the necessary models do not exist. In this paper, we describe the development of a physically based predictive model of radiation induced oxide charging. The model is based on statistical thermodynamics and electron spin resonance measurements of defects known as E' centers.

II. BACKGROUND

A. Statistical Thermodynamics

From statistical thermodynamics [4,5], it is known that equilibrium in solids is determined by minimizing the Gibb's free energy, G, where

$$G = H - T \bullet S, \qquad [1]$$

is a balance between the enthalpy (H) and entropy (S) of a solid at a given temperature (T). The enthalpy $H = E + P \bullet V$, where E is energy and $P \bullet V$ is a pressure-volume work term. In order to create a vacancy in a solid, one must supply enough energy to break all the vacant atom's former bonds. The entropy involves two terms, a configurational term and a non-configurational term. The configurational term is $S_C = k \bullet \ln(W)$ where W is the number of distinct ways of arranging the vacancies: $W = N!/((N-N_V)!N_V!)$, where N is the total number of lattice sites and N_V is the number of vacancies. (Using Stirling's approximation, $\ln(N!) = N \bullet \ln(N) - N$, $\ln(W)$ can be simplified.) From Eqn. 1, one predicts that a modest number of vacancies will be thermodynamically stable since, for a small number of vacancies, the increase in configurational entropy associated with vacancy creation more than overcomes the corresponding increase in enthalpy, resulting in a net decrease in the Gibb's energy. When the Gibb's free energy (Eqn. 1) is minimized [4,5], the concentration of vacancies, $[N_V]$, in thermodynamic equilibrium will be (in the simplest cases)

$$[N_V] = A \bullet e^{-\Delta Ha/kT} \qquad [2]$$

where ΔH_a is the activation enthalpy of vacancy formation and A is a constant which incorporates the number of available lattice sites and the effects of non-configurational entropy. (The non-configurational entropy term is temperature independent and can be large; it accounts for the increase in effective vibrational, translational, and rotational energy levels for the atoms surrounding the vacancy site.) Eqn. 2 indicates that vacancy concentration is highly temperature dependent, the higher the temperature, the greater the vacancy concentration. Rearranging Eqn. 2 yields:

$$\ln[N_V] = \ln(A) - (\Delta H_a)/k \bullet (1/T). \qquad [3]$$

0018-9499/97$10.00

B. E' Centers

Electron spin resonance (ESR) measurements are the best available technique for providing structural information about electrically active defects in oxides [6]. ESR measurements have shown that in a variety of reasonably high quality oxides the MOS oxide trapped holes and the defects known as E' centers have approximately equal densities and virtually identical spatial distributions and annealing characteristics [7-9]. The structure of the E' center defect (see Fig. 1) is that of a hole trapped on a Si atom that is adjacent to a *missing* oxygen atom; an oxygen *vacancy*. The original work linking E' centers to positive charge is well established [7-9] and it has been confirmed by several later independent studies [10-15]. It is known that post-oxidation high temperature treatments degrade the radiation hardness of the oxide partly as a result of increased positive charge trapping [16,17] at increased oxygen vacancy E' centers [7].

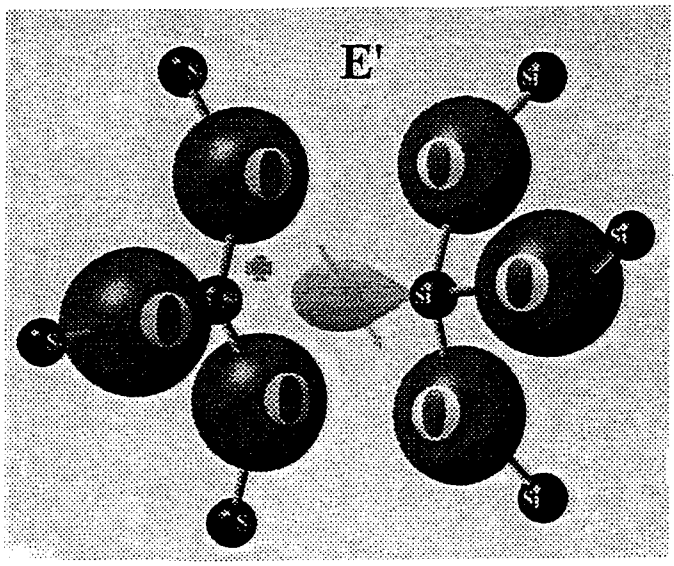

Fig. 1: Ball and stick diagram of the E' center, a hole trapped at an oxygen vacancy.

Despite the overwhelming evidence that E' centers are the dominant positive charge in radiation damaged oxides, one cannot conclude that E' centers account for all positive charge in all oxides under all circumstances. For example, Fowler-Nordheim stressing can generate anomalous positive charge that is not due to E' centers [18,19]. Also, heavily damaged oxides or micro-contaminated oxides may not exhibit close correlation between E' and positive charge [20]. Fleetwood et al. [21] have reported thermally stimulated current measurements indicating a partial compensation of positive oxide charge by trapped electrons. They report more hole trapping than electron trapping (≥2x) and that electron trapping scales with hole trapping. Thus, in oxides with charge compensation, E' density may overestimate total positive charge density by a scaling factor which, according to Fleetwood *et al.* [21], can approach a factor of two in some cases. Finally, in oxides that are not thermally grown, such as SIMOX [22] or PECVD [23], one does not necessarily observe a close correspondence between E' and positive charge.

For the purposes of this paper, we will assume that E' centers are the dominant hole traps.

C. Experimental Plan

Assuming that the dominant hole traps in thermal SiO_2 are E' centers (O-*vacancy* defects), we can replace $[N_V]$ in Eqn. 3 with [E'] and write:

$$\ln[E'] = \ln(A) - (\Delta H_a)/k \bullet (1/T_{max}), \qquad [4]$$

where T_{max} is the maximum temperature that an oxide witnesses.

If one processes oxides at a variety of temperatures and then activates the E' precursors via irradiation, one might expect (from Eqn. 4) that plots of ln [E'] vs. $1/T$ and ln $[N_{ot}]$ vs. $1/T$ would yield straight lines. Straight lines would allow extraction of the activation enthalpy, ΔH_a (from the slope), and the constant, A (from the y-intercept), for E' precursor (O vacancy) formation. ΔH_a and A can then be substituted into Eqn. 2 to predict the total equilibrium density of E' precursors, $[E']_{precursor}$, that will be present after a dominant high temperature step, T_{max}. Then, knowing E' precursor distribution and hole capture cross section, σ_h, one can predict the mid-gap voltage shift, ΔV_{mg}, that results from an incident hole fluence, η, from:

$$\Delta V_{mg} = (q/C_{ox}) \bullet [E']_{precursors} \bullet (1 - e^{-\sigma h \bullet \eta}), \qquad [5]$$

where q is the electronic charge, C_{ox} is the geometric capacitance of the oxide, and $[E']_{precursors} = A \bullet e^{-\Delta Ha/kTmax}$ (when $[N_V]$ in Eqn. 2 is replaced by $[E']_{precursors}$).

In this paper, we will first calibrate Eqn. 4 by obtaining experimental values for ΔH_a and A and then use Eqn. 5 to test the validity of the model on 10.2 eV vacuum ultraviolet irradiated oxides and ^{60}Co irradiated MOS devices.

III. EXPERIMENTAL DETAILS

Fig. 2. shows the array of 45 nm oxides used in this study; they were grown at 825°C in dry O_2 and then capped with poly-Si. Sets of oxides were then subsequently annealed for 30 min in N_2 at either 825°C, 875°C, 950°C, 1050°C, or 1100°C. After the anneal, the oxides were rapidly pulled from the furnace in order to "quench" in the equilibrium density of defects (E' centers) at the anneal temperature [4,5].

ESR measurements were performed at room temperature on a Bruker Instruments X-band spectrometer. We estimate an absolute sensitivity of $\leq 10^{11}$ /cm^2. Spin densities were determined with a TE_{104} "double" resonant cavity and a calibrated "weak pitch" spin standard. This setup allows for

absolute accuracy in determination of defect density of better than a factor of two and relative accuracy between similar measurements of ±10%. High frequency (1 MHz) capacitance vs. voltage measurements were performed at room temperature with a mercury probe.

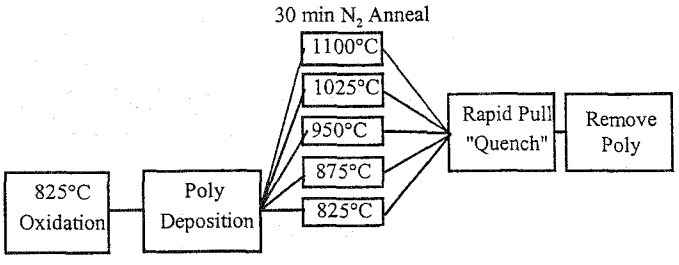

Fig. 2: Experimental array of samples used in this study.

Before any measurements were taken, the samples were cut into 20 mm X 3.5 mm rectangular bars and the poly-Si layer was removed by wet etch in a mixture of 45 g KOH / 40 ml DI / 20 ml isopropanol.

E' precursors were activated by flooding the bare oxides with holes via exposure to 10.2 eV vacuum ultraviolet (VUV) photons from a deuterium lamp while the oxide surfaces were positively biased with corona ions [24]. This procedure is detailed elsewhere [20].

The 15 nm gate oxides in the fully processed NMOS and PMOS devices used in this study were grown at 875°C and received a post poly anneal for 30 min in N_2 at 875°C. At no other time were the oxides exposed to a temperature above 875°C.

In the fully processed devices, E' precursors were activated by exposure to ^{60}Co irradiation. During irradiation, NMOS device gates were held at +5 V, PMOS device gates were held at –5V, and all other terminals on both types of devices were held at ground. ΔV_{mg} shifts were extracted from the device I_d-V_{gs} plots; these devices exhibited low interface trap density at the time of ΔV_{mg} extraction.

IV. RESULTS

A. Calibration of Model

In Figs. 3 and 4, we plot ESR measurements of ln [E'], CV measurements of ln $[N_{ot}]$, and estimates of ln $[N_{ot}]_{sat}$ (the saturation value of $[N_{ot}]$ at high hole fluence [25]), vs. $1/T_{max}$ for the array of oxides shown in Fig. 2. (As mentioned previously, the rapid pull step was performed to "quench" in the equilibrium number of vacancies at the anneal temperature [5], so that $T_{max} = T_{anneal}$.) In each case, the oxides were flooded with ~1x10^{13} holes/cm^2 with the VUV hole injection procedure. From the roughly parallel slopes of a least squares fit to the data in Fig. 3, we extract an activation enthalpy of approximately 1.5 ± 0.1 eV. This value is in agreement with earlier work [26]. In Fig. 4, ln (A) is extracted from the y-intercept of the same least squares fit to the data. We find $A \cong 4.8 \times 10^{18}$.

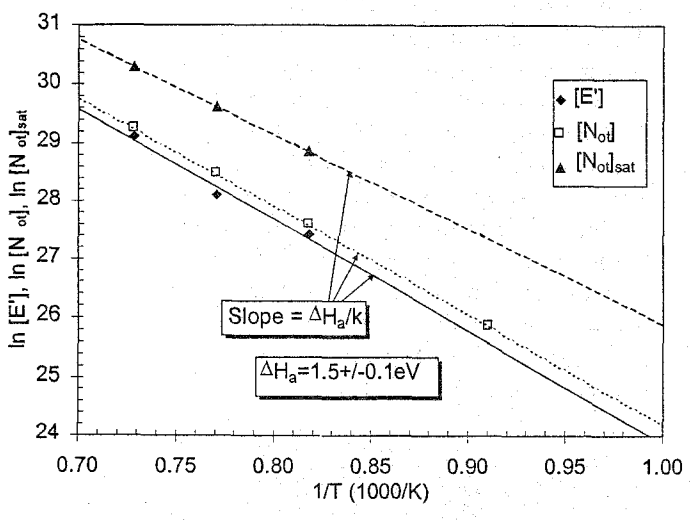

Fig. 3: Extraction of ΔH_a from slope: Plot of ln [E'], ln $[N_{ot}]$, and ln $[N_{ot}]_{sat}$ vs. $1/T_{max}$ for oxides flooded with ~1x10^{13} holes/cm^2.

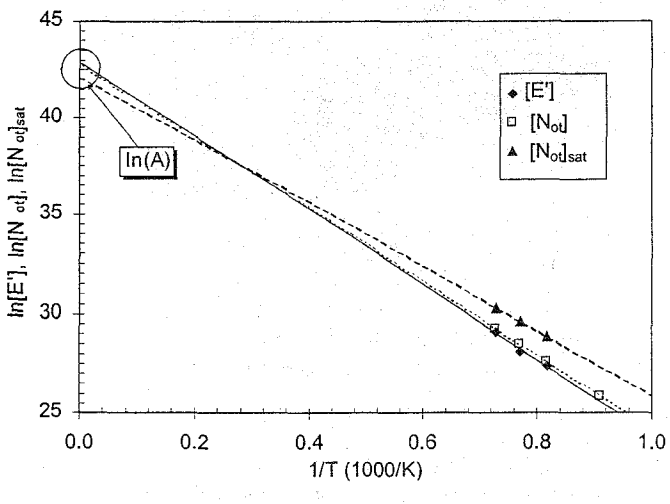

Fig. 4: Extraction of A from y-intercept: Plot of ln [E'], ln $[N_{ot}]$, and ln $[N_{ot}]_{sat}$ vs. $1/T_{max}$ for oxides flooded with ~1x10^{13} holes/cm^2.

B. Test of Model

VUV Hole Flooding

To test the predictive capability of our model, we attempt to predict for the same series of oxides, the mid-gap voltage

shift vs. VUV hole fluence, η. In Fig. 5 we plot capacitance vs. voltage measurements of mid-gap voltage shift and theoretical calculations of mid-gap voltage shift vs. hole fluence. The *theory* in Fig. 5 is a plot of Eqn. 5 with ΔH_a = 1.5 eV and $A = 4.8 \times 10^{18}$ (the parameters obtained from Figs. 3 and 4) and $T_{max} = T_{anneal}$. We also assume that E' (hole trap) centers are distributed predominantly within 10 nm of the SiO_2 interfaces [9,27-29] (the bias applied during irradiation determines whether E' centers near the Si (positive bias) or E' centers near the gate (negative bias) are filled [29]) and $\sigma_h \cong 3 \times 10^{-14}$ cm^2 [20,30-32]. Excellent quantitative agreement is obtained.

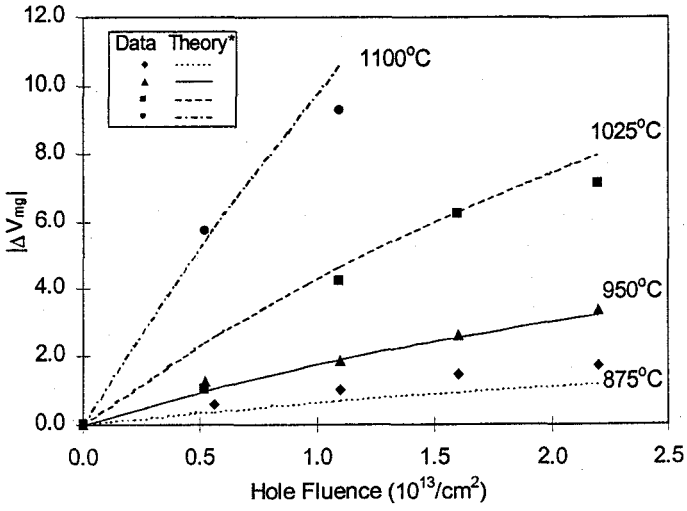

Fig. 5: Plot of experimental and theoretical ΔV_{mg} vs. VUV hole fluence.

^{60}Co Irradiation

To further test the model, a *different* set of oxides was grown to 15nm at 875°C in dry O_2, as the gate oxide of fully processed n-channel and p-channel MOSFETs. These devices were subjected to ^{60}Co gamma irradiation with the gate of the n-channel device held at +5V and the gate of the p-channel devices held at –5V; other terminals were held at ground. Fig. 6 shows the predicted ΔV_{mg} and the extracted approximate ΔV_{th} of several devices ^{60}Co irradiated to doses up to 1.2 Mrad. Immediately after irradiation, the devices were observed to have very low densities of interface traps; thus ΔV_{th} is due mainly to $[N_{ot}]$. Again, the theory curves in Fig 6. are plots of Eqn. 5 with ΔH_a = 1.5 eV, $A = 4.8 \times 10^{18}$, and $\sigma_h \cong 3 \times 10^{-14}$ cm^2, identical model parameters to those used for Fig. 5. Here we are assuming that the 875°C post-poly Si deposition anneal is the dominant temperature step (T_{max} = 875°C) that determines E' precursor density. (Note that E' distribution within 10 nm of either interface allows for significant trapping in the "bulk" of the 15 nm oxide.) For the conversion of ^{60}Co dose to VUV hole fluence, we assumed approximately 17 eV of energy is deposited per electron/hole pair [33] and ≥95% hole yield at ~3.3 MV/cm field [34]. (Note that due to recombination effects, our conversion may overestimate ^{60}Co hole yield.) Again, excellent quantitative agreement is obtained.

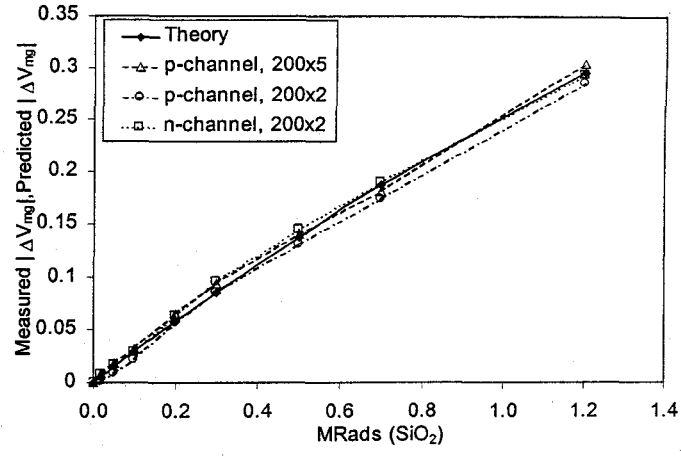

Fig. 6: Plot of experimental and theoretical ΔV_{mg} vs. ^{60}Co irradiation dose.

V. DISCUSSION

Despite the excellent quantitative agreement obtained so far, we realize that this model is not yet complete and should be viewed as first order. Issues not yet considered include pre-oxidation issues, oxidation ambient and pressure, post oxidation process damage such as plasma steps, geometry issues, etc.. In formulating this model we began with several important, but physically reasonable, assumptions. First of all, we assumed that these oxides exhibit intrinsic behavior, i.e. trapping is not dominated by contaminants. (Trapping in oxides affected by contamination probably will not be predicted by this model.) Second, we have assumed that for the formation of hole traps (O vacancies), the highest temperature step will determine the final E' precursor density.

Our third assumption is that the oxide system comes to equilibrium during the oxidation and annealing steps but not during the rapid quench step (see Fig. 2). We realize that rapid pulling is not done in either commercial or rad hard oxides, but if the samples were pulled from the furnace too slowly, equilibrium might be established at a lower temperature. At the lower temperature there would be, presumably, a lower density of defects. This would cause us to under-estimate the activation enthalpy.

While Figs. 3-6 indicate that our assumptions are valid for the current experiments, it will be necessary to consider, among other things, the kinetics of the equilibrium process, i.e. how long the system must remain at a given temperature for the density of E' precursors to come into equilibrium.

More tests are underway to study the validity of the assumptions and strengthen the basis for this model. For example, were charge compensation [21] taking place in our oxides, multiplication by a constant of order one would be required to correct our $[E']_{precursor}$ estimates.

Future refinements of the model will need to address charge trapping at the Si/SiO_2 interface (P_b centers / interface traps) and charge trapping in other MOS dielectric films such as inter-level and isolation dielectrics.

VI. SUMMARY / CONCLUSION

The excellent quantitative agreement between model and results verifies the validity of the approach and the equations. It is an essentially no adjustable parameter model: C_{ox} and T are measured, σ and E' distribution agree with that measured here and in earlier work [26], and A and ΔH_a are extracted from Figs. 3 and 4. This model is superior to a previously reported oxygen diffusion model [35]. The fit is much better and does not require the assumption that O-vacancy density change by orders of magnitude over 0.01-0.1 nm. (This assumption is physically unreasonable for a 0.2 nm diameter defect and it is in conflict with earlier work showing that $[N_{ot}]$ and [E'] density extend out to 10 nm from the interfaces [9,27-29].)

Our results are particularly significant because they represent, to the best of our knowledge, the first physically based model that allows quantitative *predictions* of radiation induced threshold voltage shifts from process parameters (in this case, the dominant high temperature step); predictions that are verified for a range of oxides processed at different temperatures and also for several MOSFET devices. Our results indicate that the lofty goal of physically based predictive TCAD models is almost certainly attainable and demonstrate that ESR is viable tool for the calibration and verification of the physically based models that will be necessary to confidently build radiation hardness into MOS gate oxides [2,36].

VII. ACKNOWLEDGEMENTS

The authors thank B. Offord, Dr. T. Oldham, Dr. H. Evans, R. Lowry, and C.J. Nicklaw for useful technical discussions, E. Kelley for providing funding for the samples, and T. Korte for technical assistance. Work at PSU was supported by Dynamics Research Corporation.

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